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Stability analysis of a continuous stirred tank reactor with an autocatalytic reaction

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STABILITY ANALYSIS OF A CONTINUOUS STIRRED TANK REACTOR WITH AN AUTOCATALYTIC REACTION

BY

DAVID ELLIOT ROSENBERG

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ABSTRACT

The basic principles of stability analysis are set forth, including the development of a mathematical model, steady state analysis, integration of the dynamic system equations, and predictions of transient responses. The equations for the mathematical model are developed for a continuous stirred tank reactor with a cooling jacket, containing an autocatalytic reaction, in unsteady state operation. These equations are numerically integrated to obtain a good picture of reactor dynamics about the steady state. State variable methods, including the classical linearization theorems and Lyapunov's Second Method, are utilized to predict bounds of stable reactor behavior. A discussion of the short comings of each method is presented. Finally the results are compared and recommendations are set forth.

APPROVAL OF THESIS

STABILITY ANALYSIS OF A CONTINUOUS STIRRED TANK REACTOR

WITH AN AUTOCATALYTIC REACTION

BY

DAVID ELLIOT ROSENBERG

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

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BY

FACULTY COMMITTEE

APPROVED: _____

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NEWARK, NEW JERSEY

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PREFACE

The name Lyapunov is known to nearly all control engineers as the developer of Lyapunov Functions and as the author of Lyapunov's Second Method. Since control theory is being used in such diverse applications as space travel, computer automation and the production of nuclear energy, specific facets and applications of Lyapunov's Second Method are explored and compared here. Once the non-linear state model for a chemical reactor is developed, it could just as easily be a model of a space vehicle in motion or of a nuclear reactor in operation. The applications presently and in the future are infinite.

Grateful acknowledgment is made to Dr. Hung T. Chen for his helpful suggestions and corrections, and to Dr. Andrew U. Meyer for his thoughtful advice.

D.E.R.

June, 1971

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INTRODUCTION

In the course of reactor design and operation, it is often necessary to determine whether the operation will be stable or unstable as well as the bounds of stable behavior. There are various methods for determining regions of stable and asymptotically stable behavior. Several of these will be explored and compared here using an autocatalytic reaction frequently found in polymer termination

$$A + R \longrightarrow R + R$$

A steady state analysis was accomplished by solving for the steady state concentrations as a function of temperature and flow rate. Steady state trajectories could then be plotted and the characteristics could therefore be examined. A dynamic system analysis was performed by various techniques. One basic approach is the numerical integration of the dynamic system equations. Linearization of the dynamic equations (8), various types of Lyapunov functions (2, 4, 8, 11), including those due to interpretations of Krasovskii's Theorem (3, 7, 9, 10), will be utilized to determine reactor stability. Finally, the methods will be compared and discussed.

REACTOR ANALYSIS BY COMPUTATION

The Mathematical Model

Consider an ideal CSTR with a cooling jacket in which there occurs the irreversible, exothermic, second order termination reaction

$$A + R \rightarrow R + R$$

If one assumes constant physical and thermochemical properties, constant coolant temperature, the reactor performance may be described by the following material balance equations for species A and R and the thermal energy balance.

$$V_R \frac{dC_A}{d\theta} = -V_R K C_A C_R e^{-\frac{\Delta E}{RT}} - Q(C_A - C_{Ai}) \quad (1)$$

$$V_R \frac{dC_R}{d\theta} = V_R K C_A C_R e^{-\frac{\Delta E}{RT}} - Q(C_R - C_{Ri}) \quad (2)$$

$$\rho V_R C_p \frac{dT}{d\theta} = -\Delta H V_R K C_A C_R e^{-\frac{\Delta E}{RT}} - \rho Q C_p (T - T_i) - UA_R (T - T_c) \quad (3)$$

The symbology used here is explained in Table I.

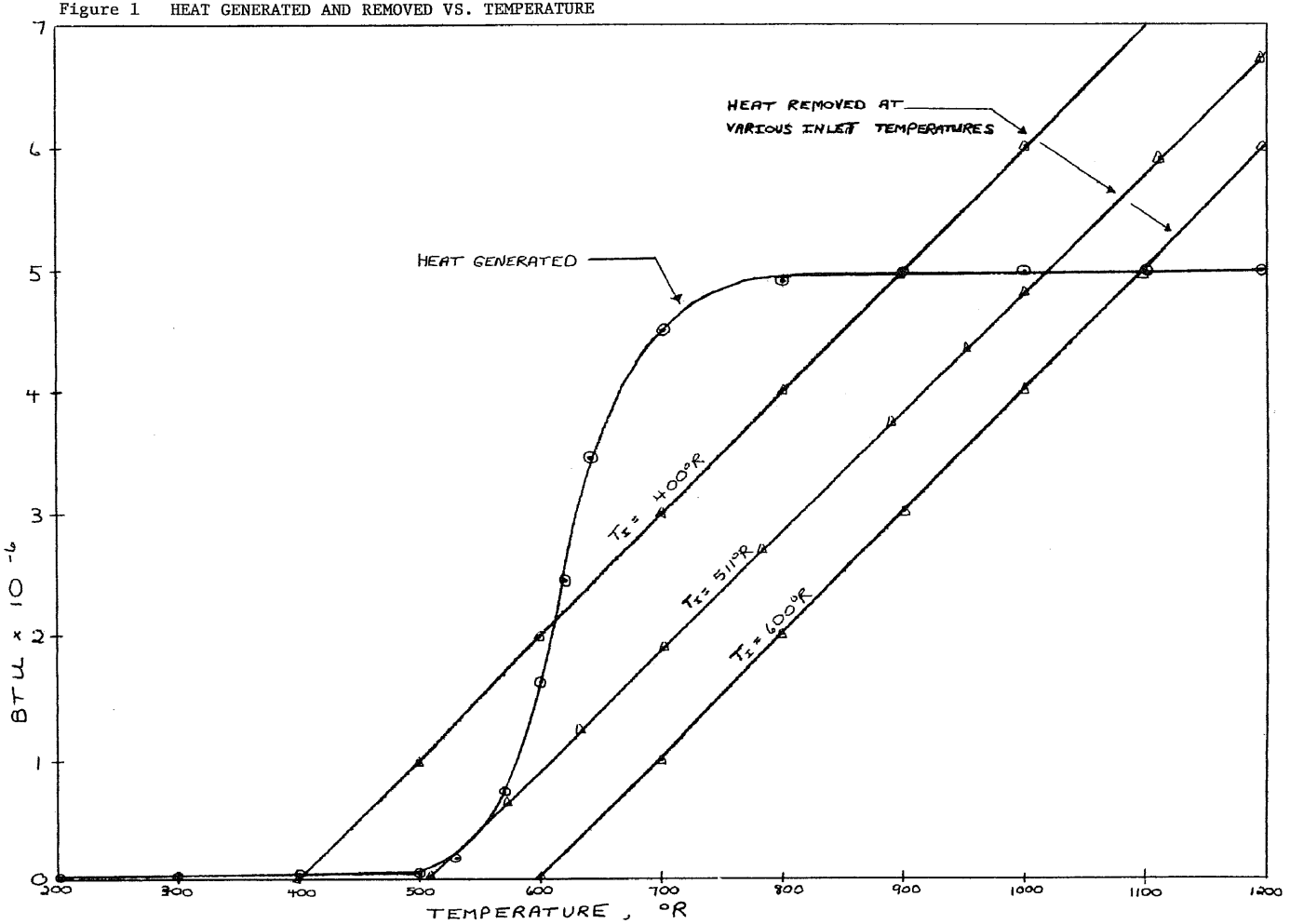
TABLE I

Symbol	Meaning	Value	
		Example 1	Example 2
ρ	Density	50 lb/ft^3	.9 grams/cc
V_R	Reactor Volume	100 ft^3	88947 cc
C_P	Heat Capacity	1 Btu/lb °R	.33 cal/cc °K
ΔH	Heat of Reaction	-5000Btu/lb	-16,400 cal/gmole
K	Reaction Constant	$10^8 ft^3/lb$ hr	$1.255X10^{12}$ cc/gmole-sec
ΔE	Activation Energy	21240 Btu/lb mole	16770 cal/gmole
U	Heat Transfer Coefficient	5 Btu/ft^2 hr °R	0 cal/cm^2 sec
A_R	Heat Transfer Area	200 ft^2	o cm^2
Q	Reactant Flow Rate	100 ft^3/hr	.593 cc/sec
T_C	Coolant Temperature	520 °R	(Arbitrary) °K
T_i	Inlet Temperature	615 °R	300 °K
C_{Ai}	Inlet Concentration, A	.2 lb/ft^3	.01 gmole/cc
C_{Ri}	Inlet Concentration, R	.2 lb/ft^3	.0001 gmole/cc
R	Gas Constant	1.987 Btu/lb mole °R	1.987 cal/gmole °K
$\bar{C}_A$	Concentration, $\frac{C_A}{C_{Ai}}$	dimension-less	dimension-less
$\bar{C}_R$	Concentration, $\frac{C_R}{C_{Ai}}$	dimension-less	dimension-less
$\bar{T}$	Temperature, T/T*	dimension-less	dimension-less
$\bar{\theta}$	Time, $Q\theta/V_R$	dimension-less	dimension-less
T*	Characteristic Temperature, $\frac{UA_R\ T_C}{\rho Q\ C_P}$	719 °R	300 °K
A_1	State Variable Constant	.139 ft^3hr/lb	.002878 cc sec/gmole
A_2	Dimension-Less Constant	.483	.00567
B	Dimension-Less Constant	1.2	1.0
D_1	State Variable Constant	5. ft^3hr/lb	100. cc sec/gmole
D_2	Dimension-Less Constant	2.23	56.13

Steady State Analysis

Equations 1, 2, 3 describe the steady state behavior of the system when the left hand sides are set equal to zero. Steady state concentrations can be found as a function of temperature by solving the first two equations simultaneously for C_A or C_R. Once the steady state concentrations are determined for given inlet conditions, the heat generation and removal terms of Equation 3 can be evaluated. For increasing steady state temperatures, the amount of heat generated will increase according the reaction rate. Above a certain temperature, however, the slope will start to decrease due to the fact that most of the species A present is reacting and this limits the reaction rate. The heat removed line is just the heat loss of the reactor due to the exit stream of heated product. These two terms are shown in Figure 1. Various inlet temperatures will cause the heat removed line to intersect with the heat generated curve at various places. The physical parameters used are listed in Table I under "Example 1". However, the reactor operation was assumed to be adiabatic in this case thus the heat transfer coefficient was set to zero. The three inlet temperature lines intersect the heat generated curve in three, two and one places. This demonstrates the existence of regions having three, two, and one steady states. Note that the existence of two or any even number of steady state points is unique to a given set of conditions as this means that the heat removed line is

Figure 1 HEAT GENERATED AND REMOVED VS. TEMPERATURE



tangent to the heat generated curve at one or more places.

By varying flow rates, steady state temperature and concentrations will vary. By solving Equations 1, 2, 3 at different flow rates, the variation of steady state temperature and concentration can be found. Various flow rates will produce one, two, or three steady states as was shown before. This method was used to produce Figures 2 and 3. The metric units in Table I were used since the region having three steady states was quite large and physically possible. In Figures 2 and 3, as the residence time in the reactor increases, the steady states increase from one to two until three. The range of residence times having three steady states is about six orders of magnitude. At still higher residence times, the number of steady states decrease from three to two until one is reached. Although Figures 2 and 3 are similar, the differences are significant. The steady state temperatures are widely separated at the high and low steady states for different inlet temperatures. This could be important if temperature were critical to the reaction. The high and low steady state concentrations are fairly independent of inlet temperature and correspond to one hundred and zero percent conversion. The constraint of material balance and positive concentrations evidently places a limit on steady state concentration that has no counterpart in steady state temperature.

Figure 2 PLOT OF STEADY STATE TEMPERATURE AGAINST RESIDENCE TIME

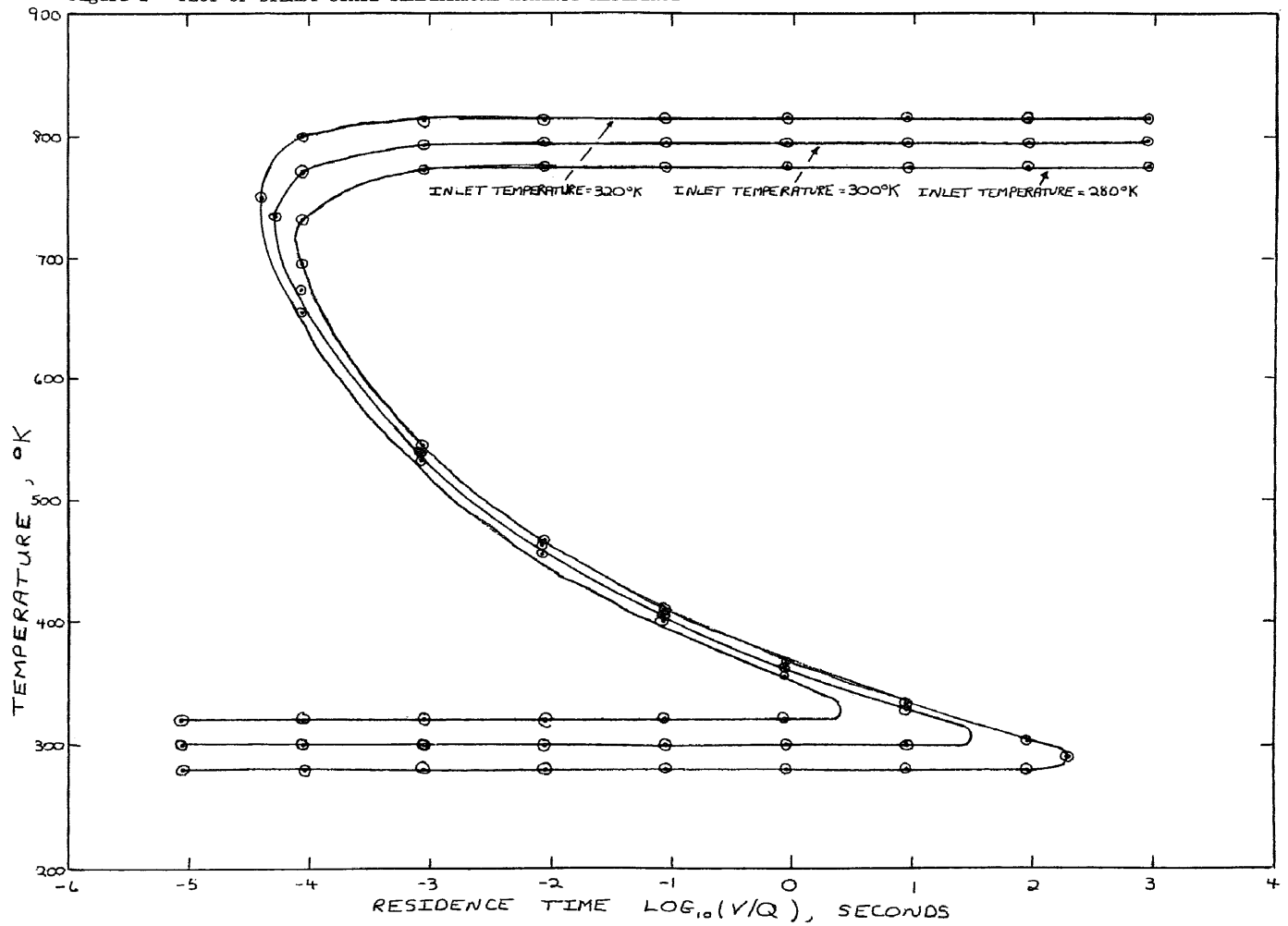
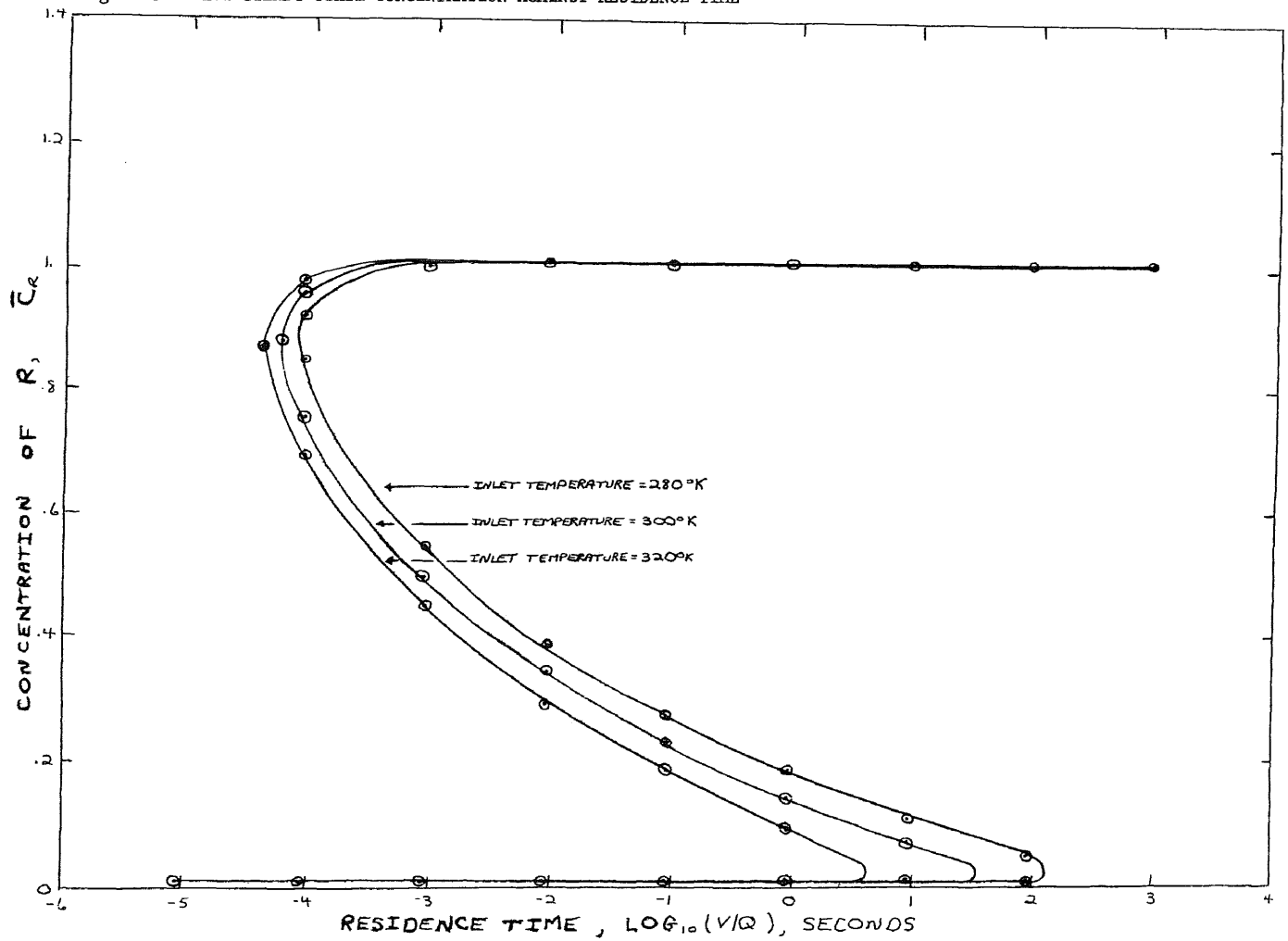


Figure 3 PLOT STEADY STATE CONCENTRATION AGAINST RESIDENCE TIME



Transient Analysis

The transient behavior of the reactor can be determined by integration of equations 1, 2, 3. Numerical integration was performed on a digital computer using the four point Runge-Kutta method, modifyed by Gill. Having chosen the Example 1 in Table I, one could then start with various initial temperatures and comcentrations and integrate the equations until a steady state point was reached or something else occured such as an instability. Different initial or starting temperatures and concentrations traced different trajectories as the system returned to steady state. Dimensionless quantities $\overline{C}_A$, $\overline{C}_R$, $\overline{T}$ were used to calculate the points, rather than the dimensioned quantities. The symbols used to obtain these values is shown in Table I. The projection of several trajectories on the $\overline{C}_R=0$, $\overline{C}_A=0$, and $\overline{T}=0$ planes is shown by Figure 4, 5, 6, respectively. The apparent crossing of the trajectory curves is not real and is due to the projection of three dimensions on two.

An attempt was made to see what effect a variation in inlet temperature or concentration would have on reactor operation. The reactor was assumed to be at steady state. Inlet temperature and concentrations were impulsed and step changed and the equations were integrated. If an inlet variable was impulsed, the systems followed as trajectory away from steady state and then returned. If the inlet variable was step changed, the system followed the same trajectory but did not return to steady state. Interestingly enough only two trajectories were traced. These are labeled ① and ② in Figure 4. This was due to the fact that the variables used were coupled, i.e. varying of any one always resulted in varying of the other two.

Figure 4 TRAJECTORY PLOT OF $\overline{C}_A$ VS. $\overline{T}$

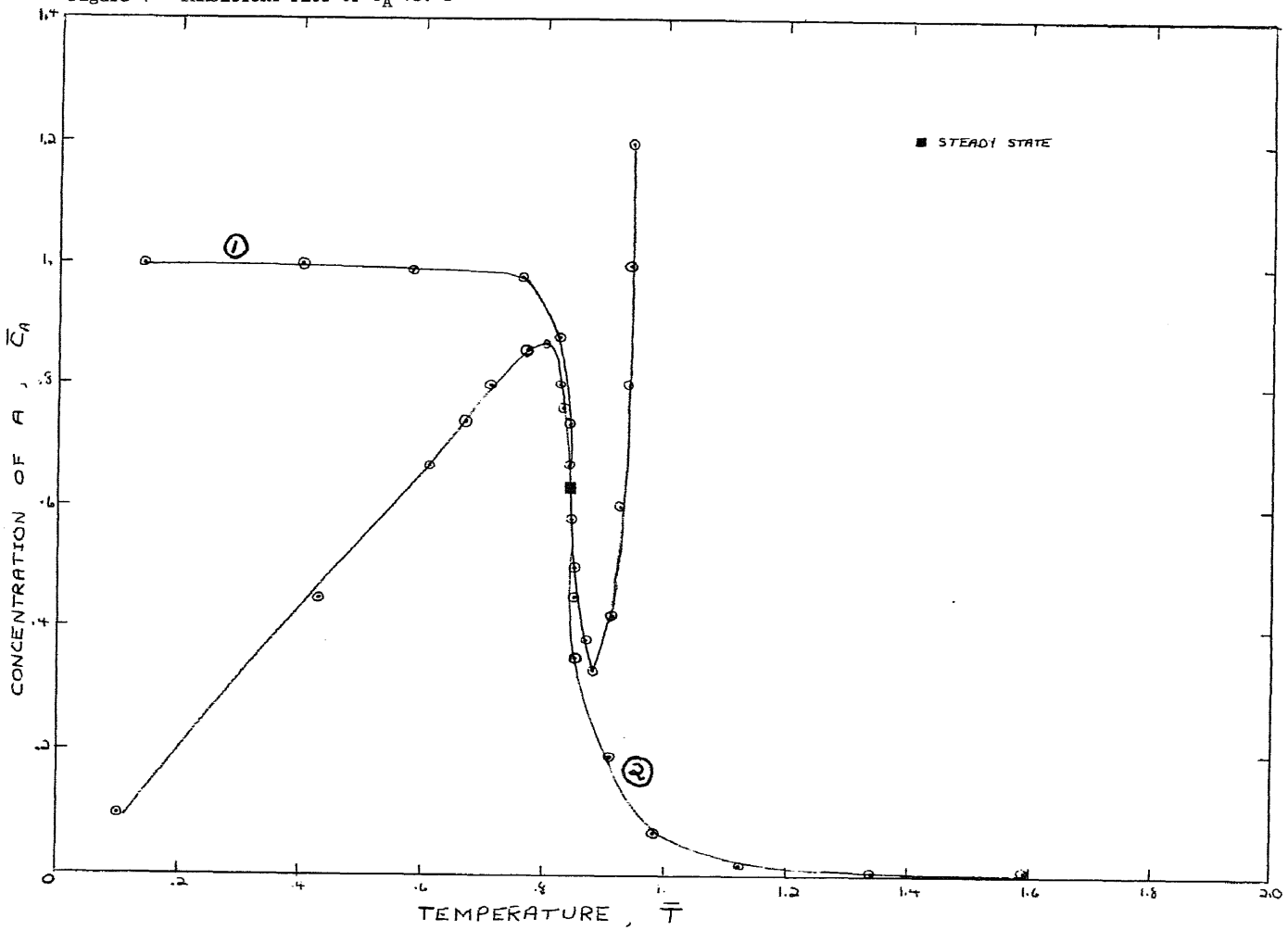


Figure 5 TRAJECTORY PLOT OF $\overline{C}_R$ VS. $\overline{T}$

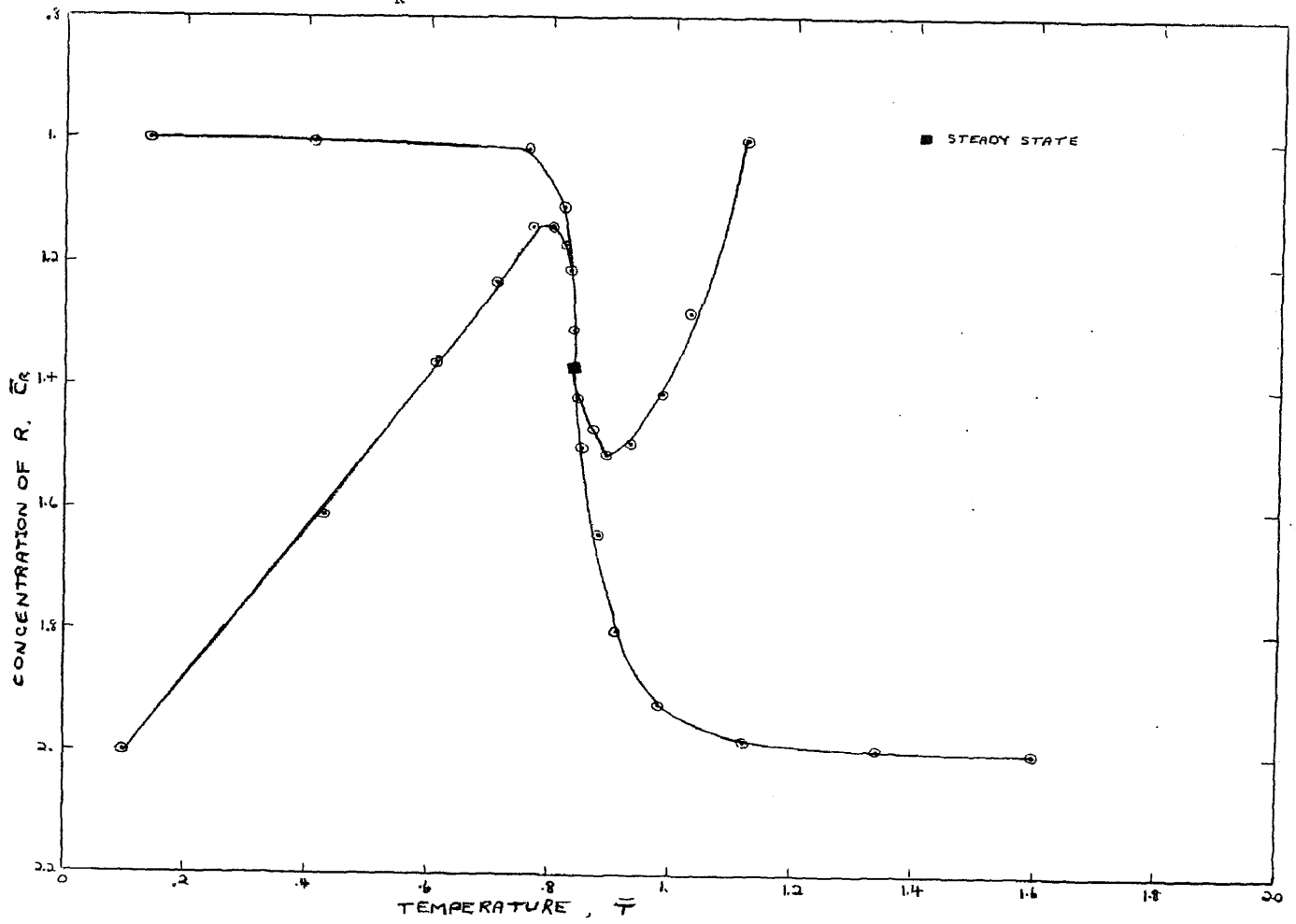
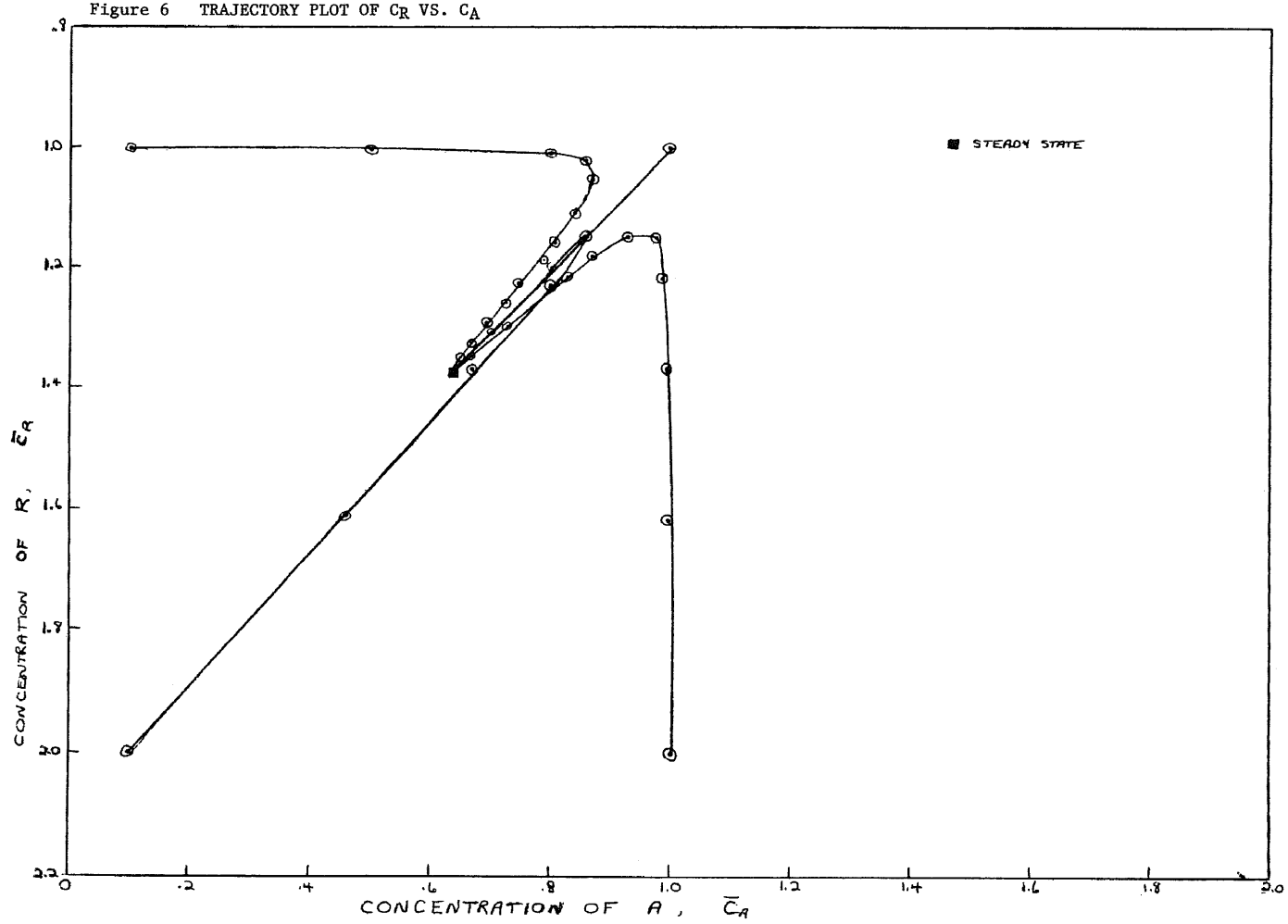


Figure 6 TRAJECTORY PLOT OF $\overline{C}_R$ VS. $\overline{C}_A$



Therefore, any control force that varied less than all three inlet conditions simultaneously would not be satisfactory for control purposes. It should be noted that there is no way to decouple the variables since this is a non-linear system. The trajectories did show that the reactor was asymptotically stable over large variations in inlet parameters. Only when initial conditions were distributed in unlikely regions of state space did the reactor begin to show instability. On the previously mentioned Figure 6, it seems that there is only a narrow corridor in the approach to steady state. At more elevated temperatures, this corridor becomes harder to reach and the reactor becomes less stable.

The Example 2 listed in Table I were chosen because the three steady state region was quite large. This was apparent on Figure 2 and 3. Just as before, numerical integration was used to determine trajectories once initial conditions were selected. Since there were three steady state points, the initial temperature and concentrations were chosen near each to see if the reactor trajectories would lead there or to another steady state point. The results were then plotted, again using dimensionless variables. Figures 7 and 8 show the trajectories projected on the $\overline{C}_R=0$ and the $\overline{T}=0$ planes respectively. The significance of the three steady states lying on a straight line is due to a material balance. The high temperature steady state, which corresponds to low $\overline{C}_A$, was not approached directly by the trajectories near it. Rather, the reactor

Figure 7 TRAJECTORY PLOT $\bar{C}_A$ VS. $\bar{T}$, 3 STEADY STATE CASE

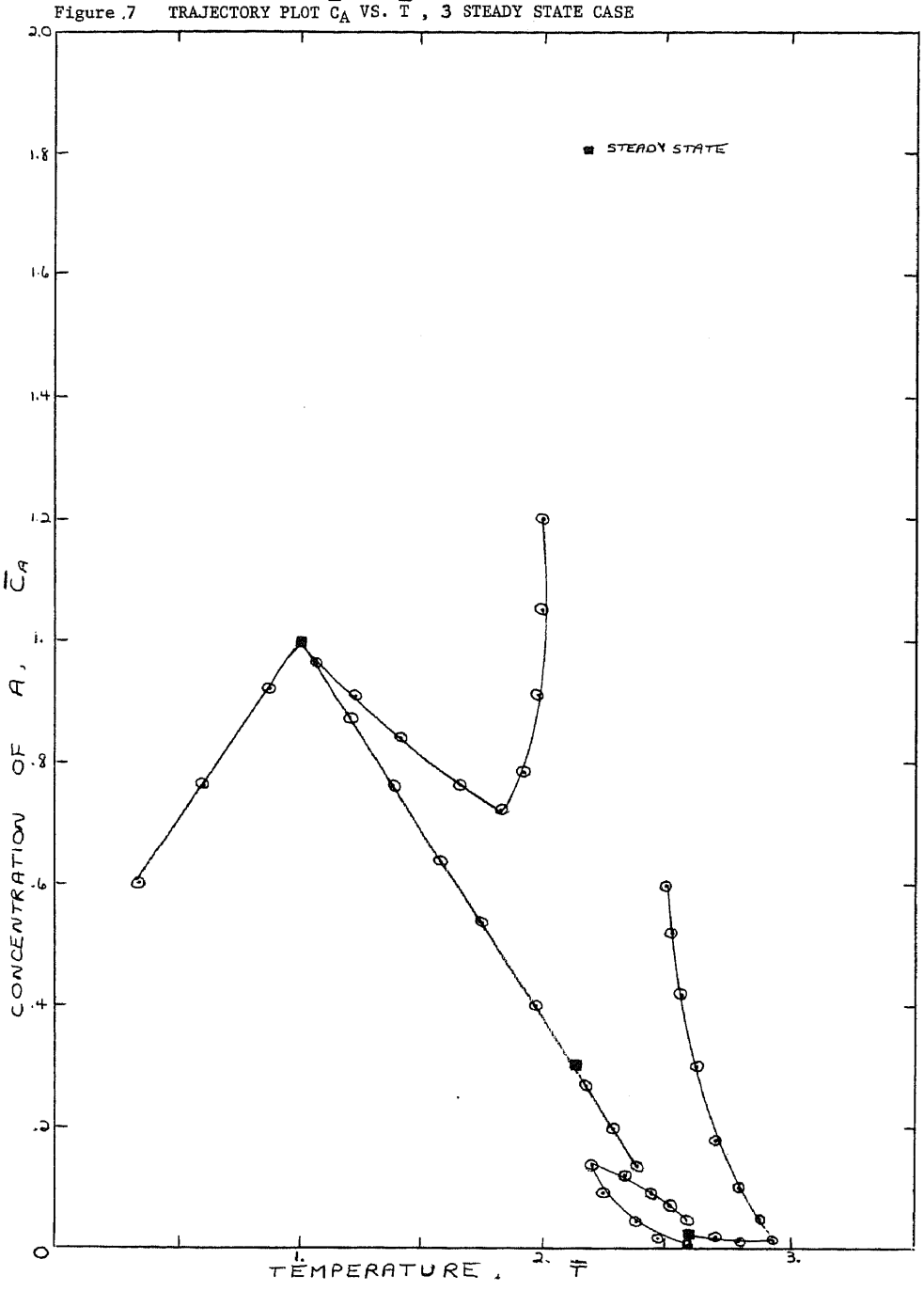
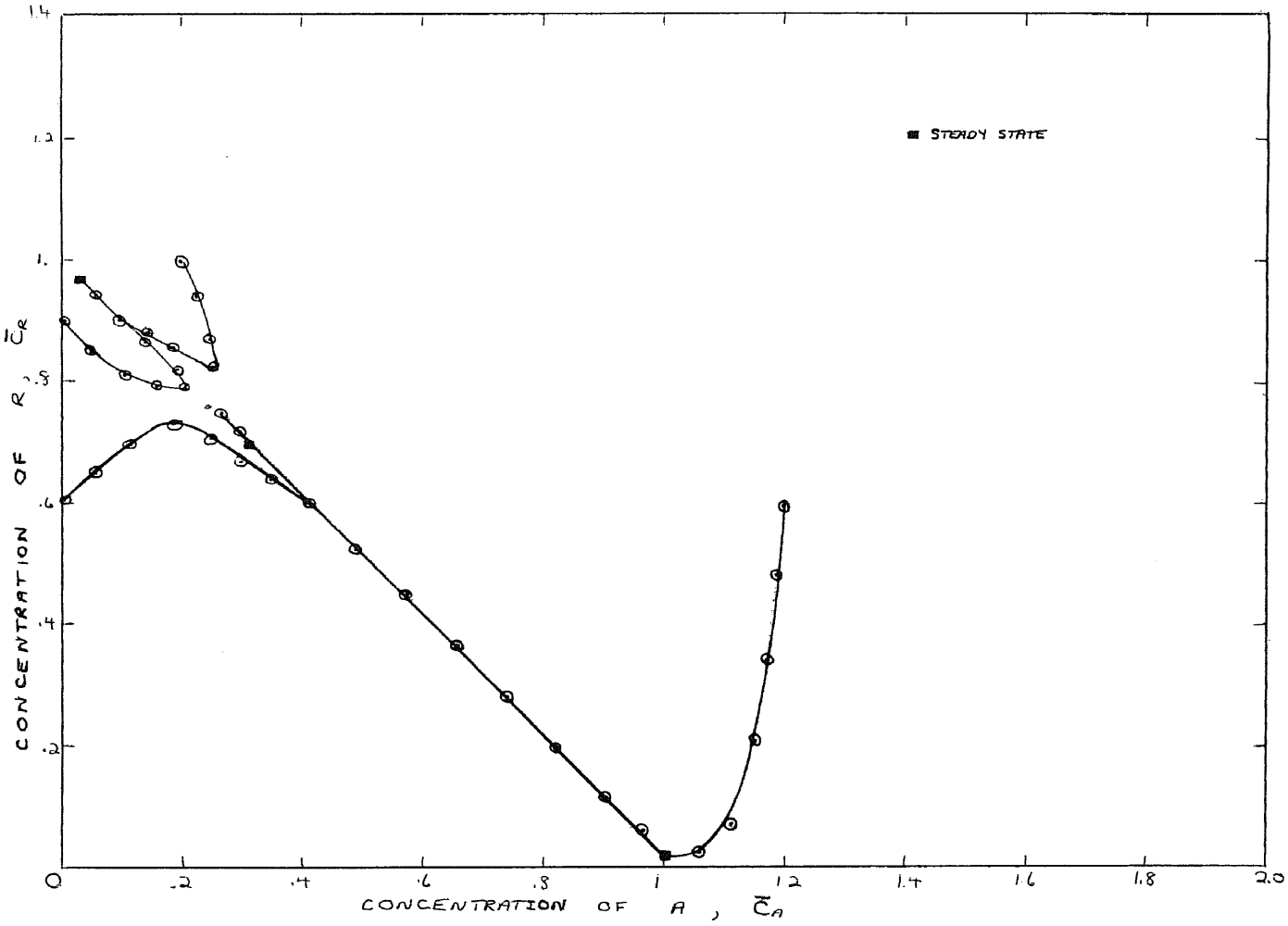


Figure 8 TRAJECTORY PLOT OF $\bar{C}_R$ VS. $\bar{C}_A$, 3 STEADY STATE CASE



system seemed to wander about the region, in some cases falling back to the lowest steady state and in some others, becoming unstable. Any trajectory passing through or near the middle steady state as though the point was did not exist. The regions of asymptotic stability are evidently relatively small for the high steady state and relatively large for the low steady state.

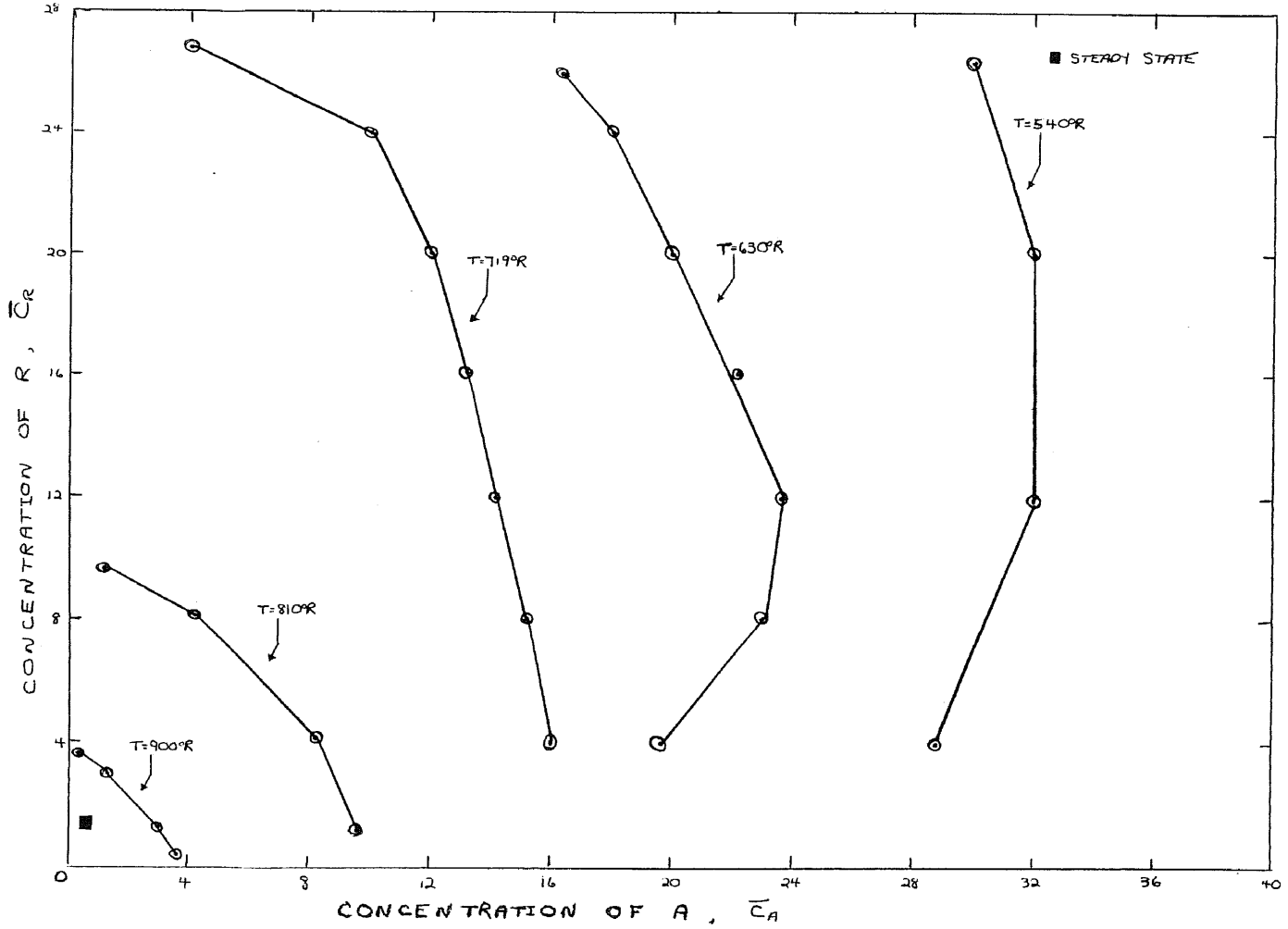
Reactor Stability by Integration

A very basic technique for determining reactor stability is that of integration of the dynamic equations. The use of numerical integrating routines on a digital computer allows system equations to be evaluated easily and quickly. This was done before in order to determine trajectories as the reactor returned to steady state. In order to determine regions of asymptotic stability, it was necessary to continue extending trajectory curves further away from the steady state point until the reactor no longer returned to steady state. These points would then be outside the region of asymptotic stability of the reactor. As the reactor trajectory passed through certain regions of state space, increasing temperature or concentration caused a larger increase in reaction rate. Since the reaction was exothermic, more heat was produced and the temperature continued to rise. The reactor trajectory was then getting further and further away from steady state. In the cases where this continued an explosion would likely result. The regions in state space where this phenomonon occurs are called unstable. Numerical integration could thus delineate the regions of state space where all trajectories starting inside the region would return at least asymptotically to the steady state point.

Although numerical integration was the most straight forward technique employed here, it was also the most time consuming, both

in man and computer time. The numerical integrating routine checked its accuracy by determining the linearity of the system. If the system was not linear enough in the time increment used, the time increment was halved and the process repeated, In doing the previous trajectory plots, the system was fairly linear. However, as it became necessary to increase concentration and temperature to find instability, the equations became extremely non-linear, due in large part to the Arrhenius Rate Law. Determining the trajectory of just one point began to take much computer time, Fortunately, a Control Data 6600 computer was available. Even so, the use of numerical integration became a costly and time consuming procedure. After much effort, points were calculated where trajectories just returned to steady state. The points were plotted on Figure 9. The Example 1 of Table I was used. Initial concentrations at five different initial temperatures were tested. The regions are seen to be decreasing and changing shape with increasing temperature. Due to the extreme non-linearity of the system, the approximate error is $\pm 10\%$. Though this error appears large, the regions are still more than double the size determined by any other method that will be attempted i.e. Linearization, Lyapunov's Second Method, Krasovskii's Theorem.

Figure 9 REGIONS OF ASYMPTOTIC STABILITY BY NUMERICAL INTEGRATION



REACTOR ANALYSIS BY STATE PLANE METHODS

The State Model

In order to apply general stability techniques, a state model must be formulated. If the dimensionless variables of Table I are utilized, Equations 1, 2, 3 become:

$$f_1(X) = \frac{d\,\bar{T}}{d\,\bar{\theta}} = A_1 r - B\,\bar{T} + A_2 \qquad \text{Where } X = \begin{vmatrix} X_1 \\ X_2 \\ X_3 \end{vmatrix} \qquad (4)$$

$$f_2(X) = \frac{d\,\bar{C}_A}{d\,\bar{\theta}} = D_1 r - \bar{C}_A + 1 \qquad (5)$$

$$f_3(X) = \frac{d\,\bar{C}_R}{d\,\bar{\theta}} = D_1 r - \bar{C}_R + D_2 \qquad (6)$$

(where A_1, B, A_2, D_1, D_2 are constants, r is the rate of reaction). Since these dimensionless equations contain constants and do not meet the requirement of state that $f(X) = 0$, a further transformation is necessary. A good choice of state variables is the deviation from steady state. Thus

$$X_1 = \bar{T} - \bar{T}_{SS}$$

$$X_2 = \bar{C}_A - \bar{C}_{ASS}$$

$$X_3 = \bar{C}_R - \bar{C}_{RSS}$$

$$t = \bar{\theta}$$

$$G(X) = r - r_{ss}$$

After Equations 4, 5, 6 are transformed, and the steady state equations subtracted, the resulting state equations are:

$$\dot{X}_1 = A_1 G (\not{X}) - B X_1 \tag{7}$$

$$\dot{X}_2 = D_1 G (\not{X}) - X_2 \tag{8}$$

$$\dot{X}_3 = D_1 G (\not{X}) - X_3 \tag{9}$$

Stability By Linear Analysis (8)

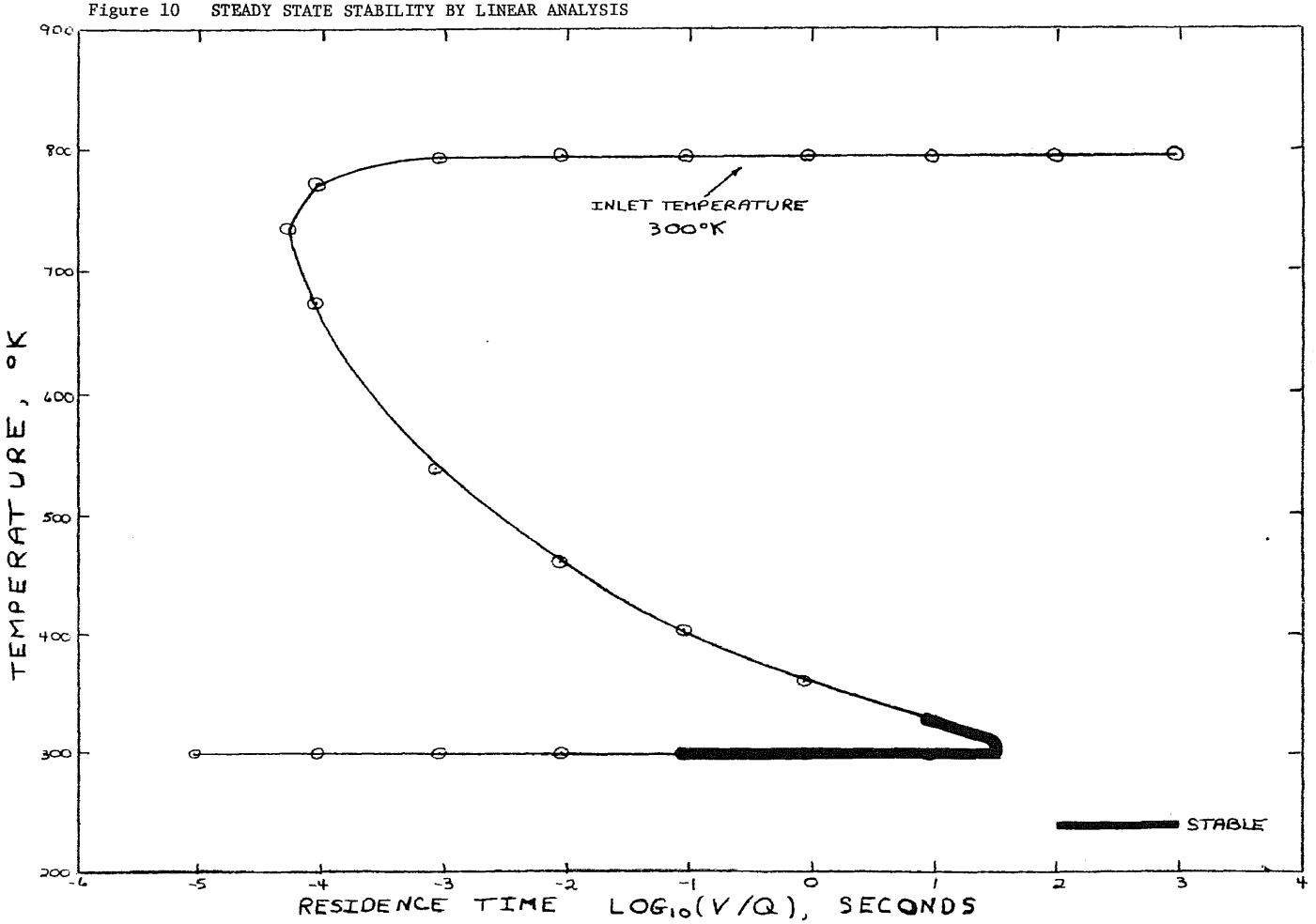
The usual technique used to determine the linear characteristics of a system when $\mathbf{f}(\mathbf{x})$ is analytic, is linearization in a Taylor series expansion about the origin. Here

$$\mathbf{A} \equiv \left(\frac{\partial \mathbf{f}}{\partial \mathbf{x}}\right)_{\mathbf{x}=0}$$

The stability of the unforced linear system can be determined by finding the eigenvalues of the $\mathbf{A}$ matrix. If all the eigenvalues are negative, the system trajectory will be composed of only decaying exponentials and the system will be asymptotically stable. If, however, any eigenvalue is positive, the system is unstable. One glaring error in this is obvious. Regardless of the initial conditions, the system will be asymptotically stable when all eigenvalues are negative. This is known as asymptotic stability in the large and can not be valid for this reactor system. The closer the system is to steady state, the better the system can be represented by a linear system. Even at steady state, however, linearization is not perfect because the reactor is still non-linear. Since the RAS will be infinite or non-existent, it was senseless to compare size. It was decided, instead, to examine the stability of the steady state points in the three steady state region. This was done by calculating the $\mathbf{A}$ matrix for the points shown on Figure 2. The state transition matrix and the eigenvalues were

calculated using a computer program found in the appendix of (5). The points which were stable were noted. The results were plotted in Figure 10. It seems that none of the high steady state points are stable and only a small section of the low ones. This may be true because of high temperatures or flow rates involved. However, numerical integration later showed that some of the high steady state points at low flow rates and more of the low steady state points are stable. Oddly enough, both linear analysis and numerical integration showed that a middle steady state point, at 332°K, is stable. This is not physically possible.

Figure 10 STEADY STATE STABILITY BY LINEAR ANALYSIS



Stability Using Linear Approximation (8)

A basic technique involves the approximation of linearity for a non-linear system. The method to be used here involves grouping the non-linear terms into a function called "g". If the linear part is asymptotically stable in the large and if the non-linear part tends towards zero near the origin, then the system must be stable near the origin. The method assumes that the contribution of the non-linear part of the system to instability is small. This is not the case for a reactor system and the results should show this.

The linear approximation theorem can be summarized as follows. Consider the non-linear system

$$\frac{d\,\mathbf{x}}{d\,t} = f(\mathbf{x})$$

Define the constant matrix $\mathbf{A}$ and the function $g(\mathbf{x})$ by

$$f(\mathbf{x}) = \mathbf{A}\mathbf{x} + g(\mathbf{x})$$

If $\frac{d\,\mathbf{x}}{d\,t} = \mathbf{A}\mathbf{x}$ is asymptotically stable in the large, and if

$$\lim_{\|\mathbf{x}\| \to 0} \frac{\|g(\mathbf{x})\|}{\|\mathbf{x}\|} = 0$$

The system is therefore asymptotically stable at the origin. The double bars signify the norm of a vector.

Using Equations 7, 8, 9, the following is obtained.

$$\begin{bmatrix} \dot{X}_1 \\ \dot{X}_2 \\ \dot{X}_3 \end{bmatrix} = \begin{bmatrix} -B & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} X_1 \\ X_2 \\ X_3 \end{bmatrix} + \begin{bmatrix} A_1 \\ -D_1 \\ D_1 \end{bmatrix} G$$

The eigenvalues of the (A) matrix are obviously all negative. Thus, the linear system is asymptotically stable in the large. The regions of asymptotic stability (R.A.S.) predicted by this theorem depend upon the region of state space where the limit of the norm of the rate expression g( ) divided by the norm of approaches zero as the norm of approaches zero. The results obtained were deviations from steady state as follows (Using the Example 1, Table I).

Temperature	± 10.2 °R
Concentration A	± .041 lb/ft^3
Concentration R	± .019 lb/ft^3

The results were quite insignificant compared with the other methods used here. The real problem involved the rate expression g( ). Since it contained the Arrhenius Rate Law and the product of concentrations C_A and C_R, it was the sole cause of instability and nonlinearity for this system. The attempt to deal with it as a trival quantity was doomed to failure.

Formulation of Lyapunov Functions

In previous works (1-4, 6-11), Lyapunov's Direct Method is employed to find regions of asymptotic stability. Various techniques are used to formulate and apply Lyapunov functions. Briefly, Lyapunov's Direct Method can be summarized as follows. Consider a system characterized as follows:

$$\frac{d\,\underline{x}}{d\,t} = \underline{f}(\underline{x}) \qquad \text{with} \qquad \underline{f}(0) = 0$$

Suppose there exists a scalar function $V(\underline{x})$ which for some number $\varepsilon>0$ satisfies the following in the region $||\underline{x}|| \leq \varepsilon$.

a. $V(\underline{x})>0 \qquad$ for $\underline{x} \neq 0$

b. $V(0)=0$

c. $V(\underline{x})$ has continuous partial derivatives with respect to $\underline{x}$

d. $\frac{d\,V}{d\,t} < 0$

Then the system is asymptotically stable at the origin.

Stability by Calculating the Time Derivative

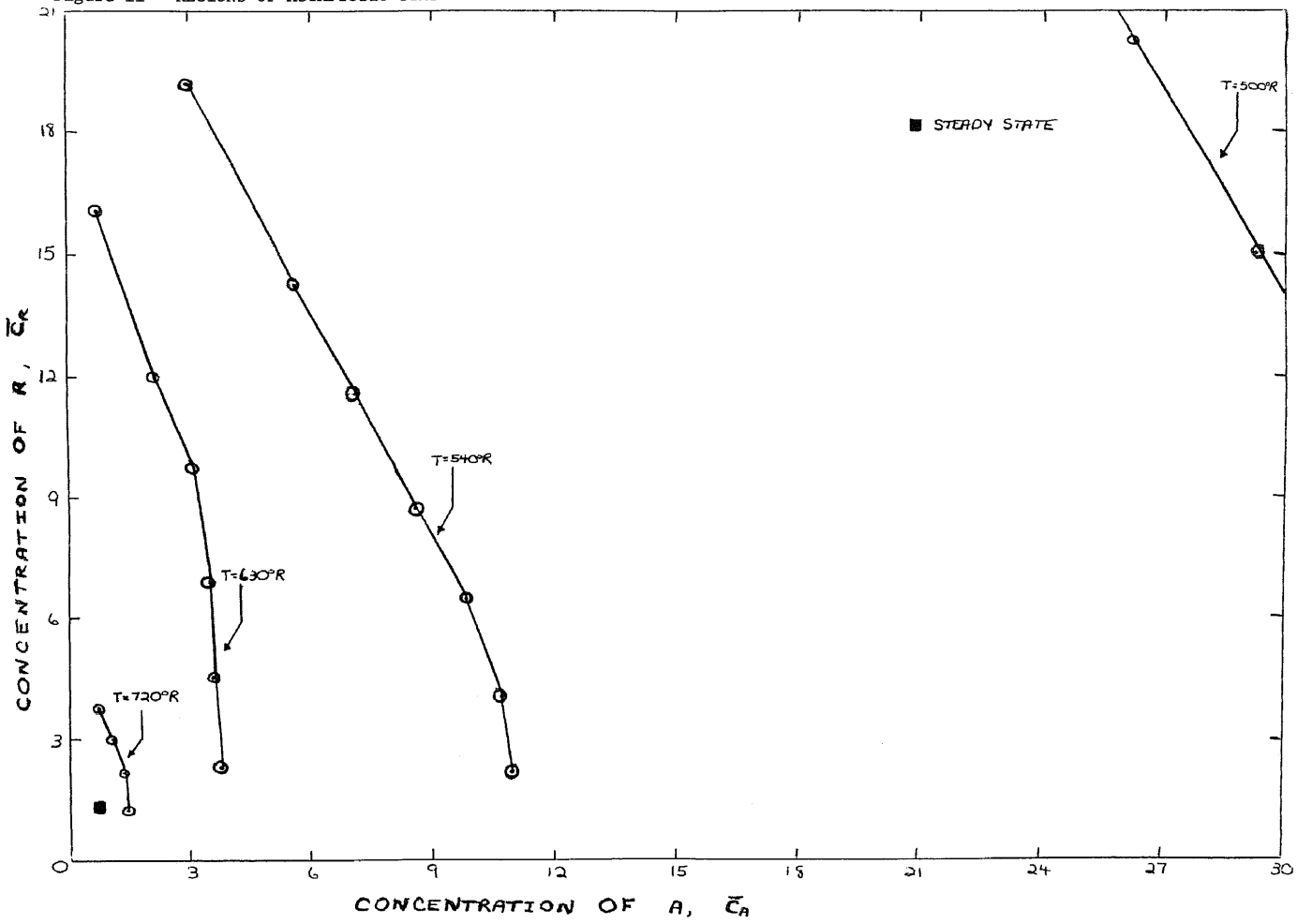
An early and general method used to apply Lyapunov functions can be found in (8). Briefly, this method involves the formulation of a Lyapunov function and the computation of its time derivative using the chain rule formula

$$\frac{d\,V}{d\,t} = \left(\frac{\partial\,V}{\partial\,x}\right)^T f(x)$$

If this derivative is negative for all points in and on the Lyapunov function, a larger Lyapunov contour can be tested. The smallest contour which has a point at zero time derivative will define the area of asymptotic stability where all trajectories will return to the origin. Application of this theorem proved difficult. Firstly, a Lyapunov function had to be selected. There were infinite possibilities and each Lyapunov function had a different in shape. Though there were no restrictions on the Lyapunov functions as with other methods (7-10), no guide was available for choosing a function for a chemical reactor system either. After several possible Lyapunov functions were tested, the function which yielded the largest RAS was the one which included both concentrations and the temperature squared as state variables in one of the terms. This was probably due to the effect of the rate expression on the system. Each Lyapunov function had to be tested for a negative time derivative

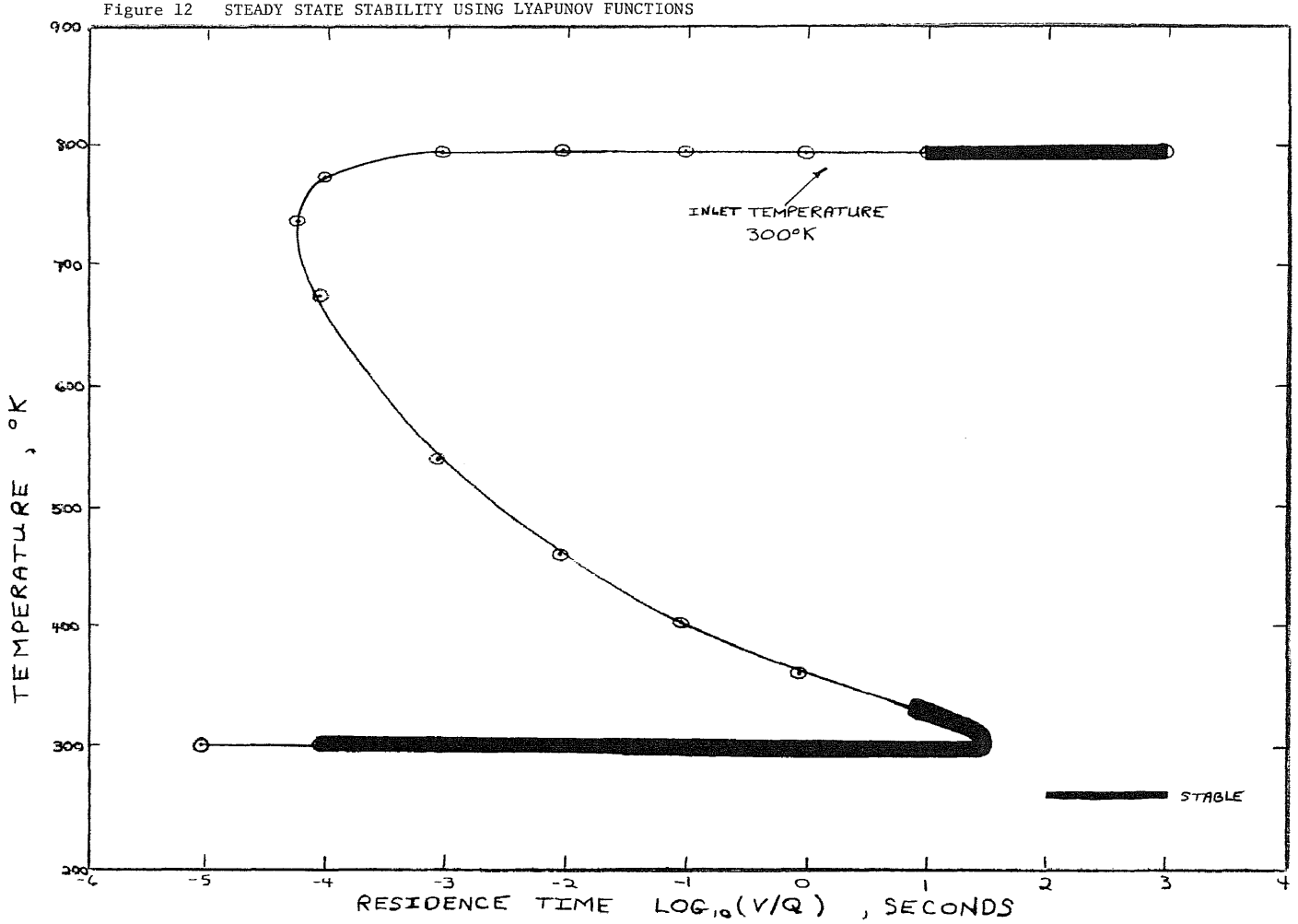
at a grid of points. The computer program which was used, tested each contour at twenty points spaced over all four quadrants of the concentration plane. Each function was evaluated at five distinct temperature intervals. The largest contour $V(\not{x})=K$ to have all points with a negative time derivative was noted for each Lyapunov function. These contours were plotted in Figure 11. However, the plot be must qualifyed. It was realized that no physical reactor can have negative concentrations during either steady or unsteady state operation. Therefore, no reactor can have a trajectory passing through those areas of state space corresponding to a negative concentration. All trajectories starting in regions of positive concentration must stay there. The restriction of a Lyapunov function having all points in a negative time derivative zone was then relaxed somewhat. Only points on the Lyapunov function which corresponded to positive concentrations were tested for a negative time derivative. What the situation was at other points was irrelevant since the reactor system could never get there! This assumption resulted in roughly 50% increases in the RAS. In Figure 11, these contours are seen to vary in shape and size as the temperature changes. Note that there is only one steady state point present. This is due to the fact that the Example 1 of Table I was used for this calculation. The limits on the contours do not extend to the axis because the system is very stable in these regions as the rate term is a function of both concentrations.

Figure 11 REGIONS OF ASYMPTOTIC STABILITY BY LYAPUNOV TIME DERIVATIVE METHOD



The three steady state region was also investigated but in a slightly different manner. Instead of seeing how big the regions of asymptotic stability were, it was decided to see which steady state points had any regions at all. This was accomplished by taking points $\pm$ .01% about a steady state point and seeing if all the points had a negative time derivative. This was done for each steady state point found on the inlet temperature equals 300°K curve in Figure 2. This was how Figure 12 was constructed. The steady state points which were asymptotically stable within the small area selected are labeled stable, although it is really stable in the small. This plot is in sharp contrast to Figure 10 where the points were either unstable or stable in the large. In Figure 12 the low steady state is stable over flow ranges 3 orders of magitude more than that of Figure 10. Also the high steady state is stable for a variation in flow rate. One middle steady state point, that at 332°K had a RAS. Numerical integration yielded the same results as that shown in Figure 12. It was completely baffling how a middle steady state point not only was stable itself but also had a small region of asymptotic stability around it. Evidently the instability of the point was smaller than the truncation and propogation error of the fifteen decimal place word on the CDC 6600 used for all calculations.

Figure 12 STEADY STATE STABILITY USING LYAPUNOV FUNCTIONS



Stability Using an Early Krasovskii Theorem

A limited region of asymptotic stability can be found by an early interpretation of Krasovskii Theorem (7), briefly summarized as follows. The non-linear system

$$\frac{d\,x}{d\,t} = f(x), \qquad f(0)=0$$

is asymptotically stable at the origin if the matrix

$$F(x) = \frac{\partial f(x)}{\partial x} + \left(\frac{\partial f(x)}{\partial x}\right)^T$$

is negative definite for all x; furthermore,

$$V(x) = f(x)^T f(x)$$

is a Lyapunov function.

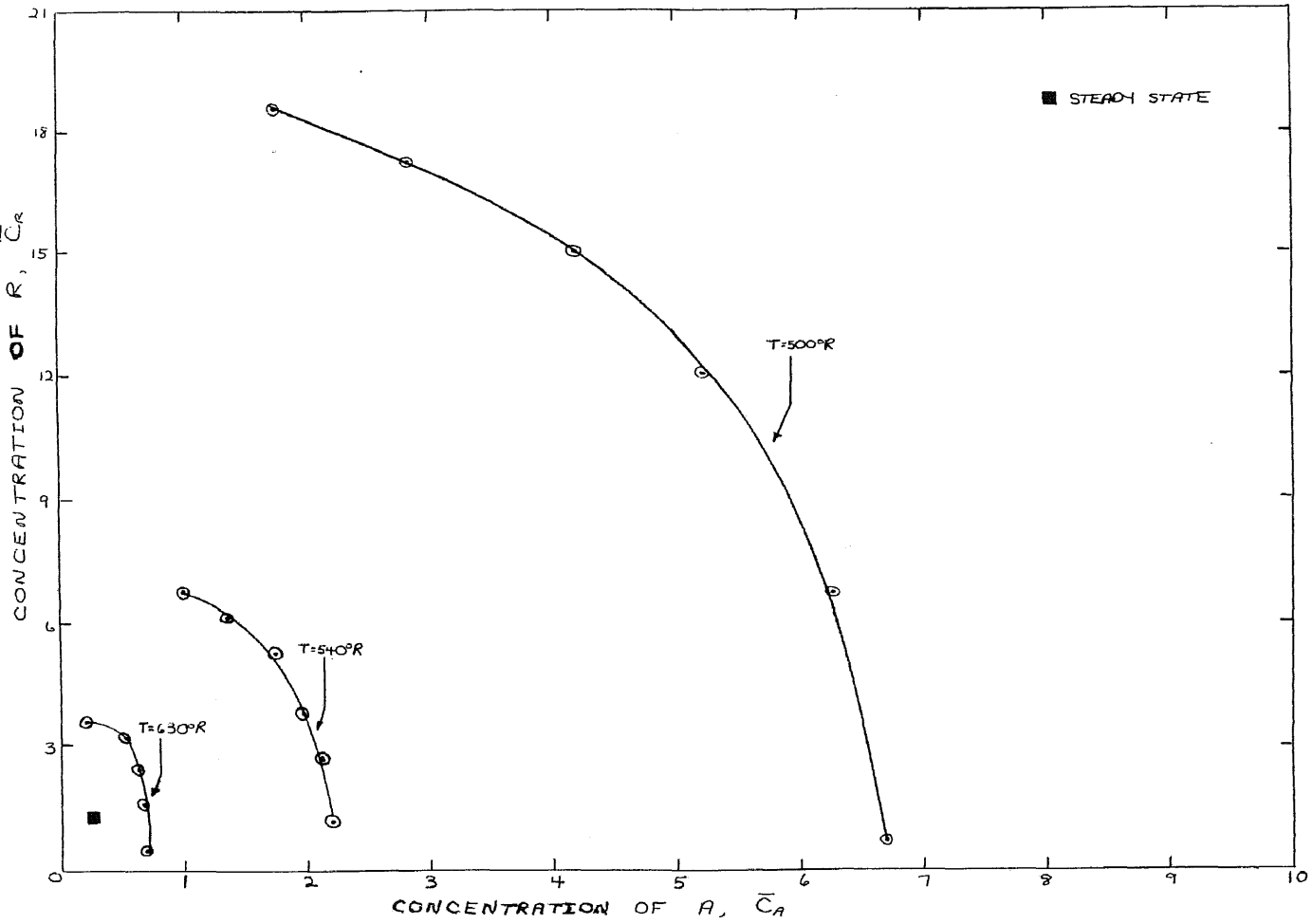
Utilizing equations 7, 8, 9, $f(0)=0$ since $G(x)$ is the deviation of the rate from steady state.

$$\frac{\partial f(x)}{\partial (x)} = \begin{bmatrix} -B+A_1G_1 & A_1G_2 & A_1G_3 \\ -D_1G_1 & -1-D_1G_2 & -D_1G_3 \\ D_1G_1 & D_1G_2 & -1+D_1G_3 \end{bmatrix}$$

G_1, G_2, G_3 are the partial derivatives of G with respect to X_1, X_2, X_3. It should be noted that the Lyapunov function is unique in this

case. It is just $f_1^2+f_2^2+f_3^2$. Certainly, there is no problem formulating the Lyapunov function. However, due to the fact that various Lyapunov functions cover various areas of state space, the RAS determined here should be very conservative. A computer program was formulated to calculate points on a Lyapunov function $V(\vec{x})=K$. A grid of twenty points, five in each concentration-concentration quadrant were tested to see if $\dot{V}(\vec{x})$ was negative definite. If it was, a larger K was used to calculate the Lyapunov function and the process repeated. The largest $V(\vec{x})=K$ to satisfy the constraints was plotted on Figure 13 at various temperature intervals. The Example 1 of Table I was again used to generate the one steady state region. The Lyapunov functions generated were ellipsoidal in shape and expanded with decreasing temperature. The ellipsoidal shape is due to the squaring of the state variable expressions. In this case, the attempt was again made to increase the RAS by only testing the constraints on areas of positive concentration only. Small increases were noted in the RAS at two of the temperatures shown. This was probably due to the fact that the functions were ellipsoidal and probably violated the constraints in several quadrants at about the same distances from steady state.

Figure 13 REGIONS OF ASYMPTOTIC STABILITY USING AN EARLY KRASOVSKII THEOREM



Stability Using the General Krasovskii Theorem

Luecke and Mc Guire gave a superior interpretation of Krasovskii Theorem (10). The non-linear system

$$\frac{d\,x}{d\,t} = f(x), \quad f(0) = 0$$

is asymptotically stable at the origin if there exist constant, symmetric, positive definite matrices P and Q such that

$$F(x) = \left(\frac{\partial f}{\partial x}\right)^T P + P\frac{\partial f}{\partial x} + Q$$

is negative definite for all x; furthermore,

$$V(x) = f^T P f$$

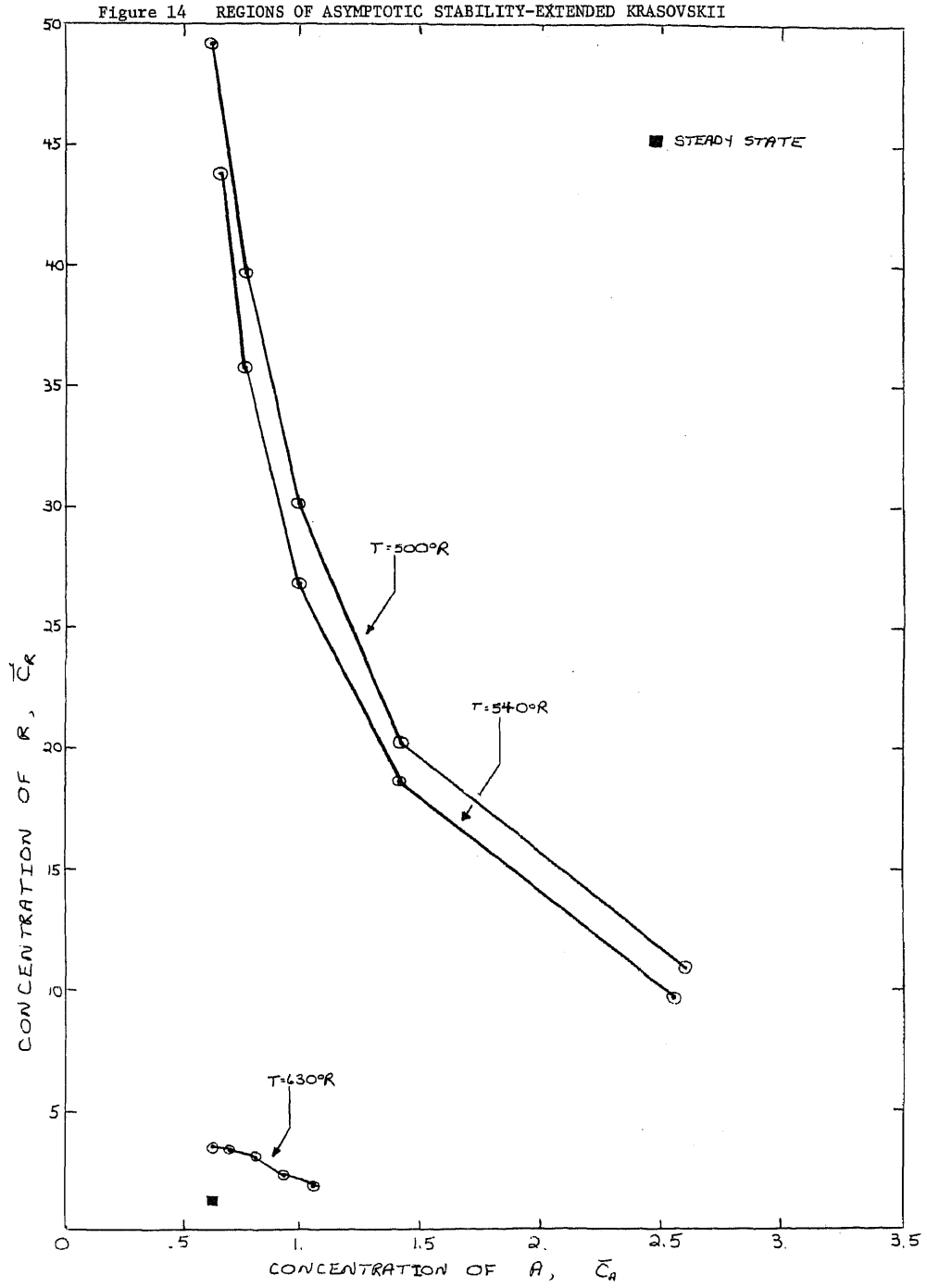
is a Lyapunov function. Luecke and Mc Guire show that astute choice of the matrix P, when using Krasovskiis Theorem, can significantly enlarge the resulting stability region. The whole draw back is in choosing the right matrices in order to enlarge the RAS. As suggested by Luecke and Mc Guire, a P matrix was chosen in an attempt at normalization of the state variables. It was assumed that the same type of normalization would work here with three state variables as it did in their case with two. This approach yielded a P matrix of

$$\begin{bmatrix} 1.79 & 0 & 0 \\ 0 & 4.73 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

It should be noted that the resulting Lyapunov function is similiar

to the one formulated in the previous section except that the orientation about the steady state is different. In other words, the f_1^2, f_2^2, f_3^2 of the previous section are multiplyed by constant terms. No cross products were attempted because there was no way to determine which would be beneficial and also because some might cause $V(\mathbf{X})<0$ for some $\mathbf{X} \neq \mathbf{0}$, invalidating the entire Lyapunov function. The matrix $\mathbf{Q}$ proved easy to choose. Before adding in $\mathbf{Q}$, F_{11} was negative, F_{22}, F_{33} were positive and the rest of the matrix was zero. Thus, very large values of Q_{22} and Q_{33} could be used to maintain $\mathbf{F}$ being negative definite. The real constraint was F_{11} being negative. Once the Lyapunov function $V(\mathbf{X})=K$ was calculated, the computer checked each of twenty points to ensure that $\mathbf{F}$ was negative definite and K was incremented until points were in violation of the constraint. As before, the Example 1 of Table I was used. The largest Lyapunov functions are plotted in Figure 14. The resulting shapes are diamond-like. It was attempted to enlarge the RAS by ignoring points in the other three quadrants not shown on the graph. Probably due to the fact that the state variables were normalized, the constraints were being violated by the points in all the quadrants at about the same distance from steady state. This procedure was then abandoned.

Figure 14 REGIONS OF ASYMPTOTIC STABILITY-EXTENDED KRASOVSKII



CONCLUSION

It has been shown that the operation of a reactor in a three steady state region will be stable at best, at the high and low steady state and unstable at the middle steady state. The fact that the high steady state may show stability can be very useful. For instance, a low inlet temperature could be used in conjunction with a controller to keep a high conversion at a high flow rate with comparatively little expenditure of energy. A region of two or even four steady states is a physically unlikely situation in that the heat removed line must be tangent to the heat generated curve in one or more places. Regions of five steady states were found on calculating the graphs of steady state temperature and concentration against residence time. However, the two steady states that were found lying below inlet temperature had concentrations of species A greater than inlet. Therefore, these were mathematical solutions only and were not plotted.

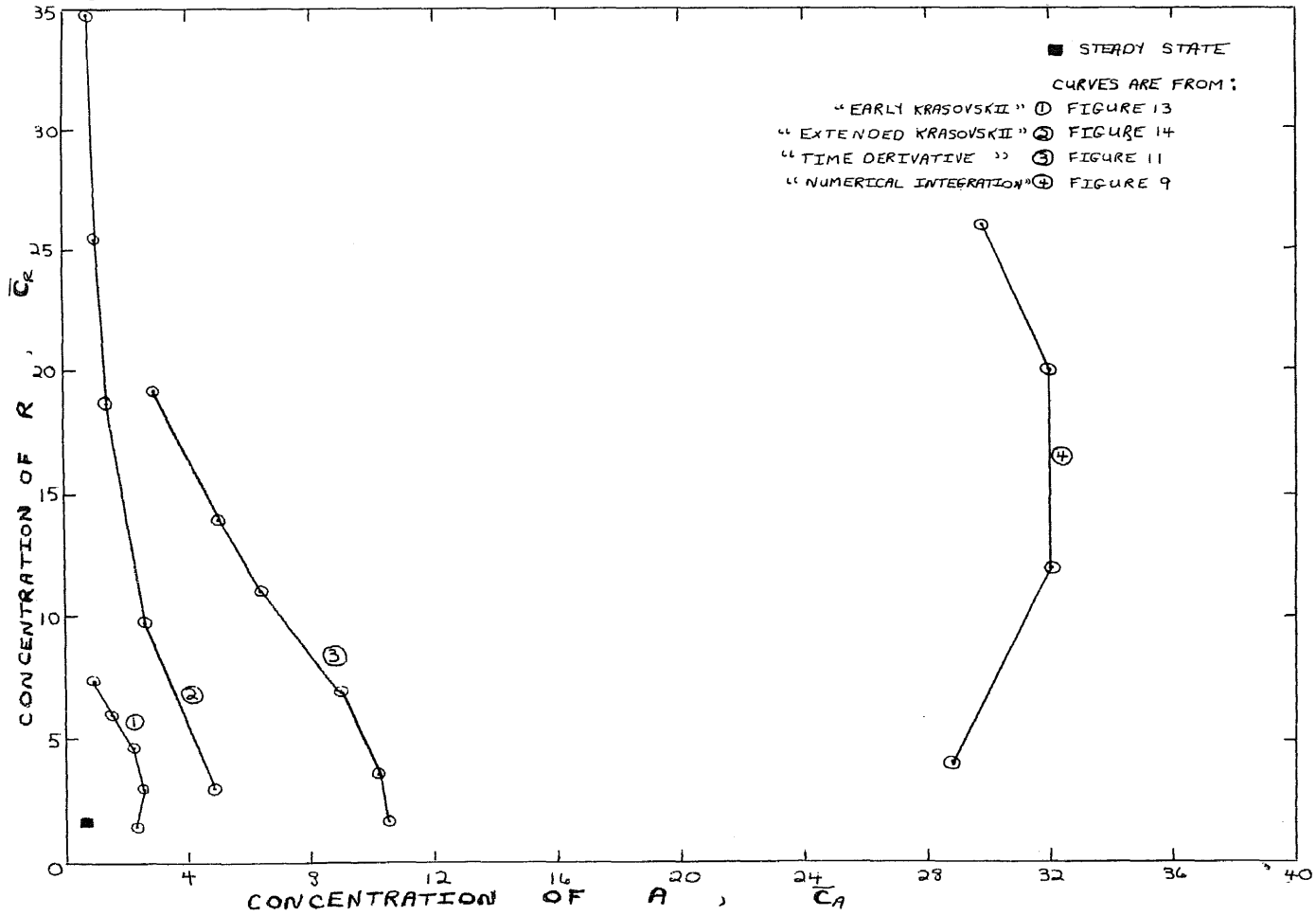
Of all the techniques used to determine reactor stability, numerical integration gave the largest and probably most accurate picture of reactor stability and dynamics. There are many reasons for this. The region of asymptotic stability is larger than that area of state space covered by a given Lyapunov function having a negative time derivative. Since Lyapunov functions are a type of energy function, any trajectory having the littlest increase in energy as defined in the function will be beyond the scope of this

approach. However, there is no available technique to delineate areas of state space having a non-negative time derivative which are stable with respect to the origin. Besides being limited in scope, Lyapunov functions are by no means unique to a given system. Various functions will cover various areas of state space. The Lyapunov functions formulated here varied widely in shape. The Lyapunov function used in calculating the time derivative and that used in satisfying the early Krasovskii Theorem were typical. Both were ellipsoidal in shape. The resulting Lyapunov function formulated using Luecke and Mc Guire's approach was almost a diamond. These are shown in Figure 15.

The linear approximation theorem and linear analysis gave very poor results for this reactor system. This was due to the fact that the instability in the reactor is caused by the Arrhenius Rate Law. The higher the temperature rises, the more unstable and non-linear the system becomes. Thus the approximation of linearity for this system is not good for determining stability.

Upon reviewing the various techniques for employing Lyapunov functions, several things became apparent. First of all, both interpretations of Krasovskii theorem limit the possible types of Lyapunov functions. In the restricted Krasovskii Theorem, the Lyapunov function is unique, i.e. it is just the product of the transpose of the f matrix and itself or $f_1^2 + f_2^2 + \ldots . f_n^2$ where n is the

Figure 15 REGIONS OF ASYMPTOTIC STABILITY BY DIFFERENT METHODS AT 540°R



number of state variables. Even in the extended Krasovskii Theorem, the Lyapunov function is limited to linear combinations of the previously mentioned terms and their first order cross products. The method of calculating the time derivative by the chain rule $(\frac{\partial V}{\partial x})^T f(x)$ enables one to pick Lyapunov functions without any restrictions other than those of Lyapunov. For this system, this unrestricted ability to pick Lyapunov functions made all the difference in the world. By trial and error, a Lyapunov function was found that most closely characterized the total energy of the system. Thus it gave a larger region of asymptotic stability than anything possible using Krasovskii techniques. Since the temperature and concentrations used here were all inter-related, it seems logical that second order cross products be included in any attempt at characterizing the total energy of this system. What apparently is lacking todate is a study of the inter-relationship of a given Lyapunov function and the type of system that it represents.

RECOMMENDATIONS

Despite the multitude of methods available to predict non-linear system response, the most accurate and uncomplicated method remains numerical integration. For linear systems, state variables are a blessing. They allow an analytic analysis of system response. Effects of distrubances and control forces can be found easily, especially when the state variables are decoupled from one another. However, state methods were of little use here. Linearization of this reactor system yielded very poor results. Applications of Lyapunov's Second Method fared not much better. Most methods employed here required computer programs. As long as such programs are necessary, numerical integration should be employed. Routines are already written which make numerical integration more accurate than any other method available. As time progresses, the advent of faster and cheaper digital hardware, combined with prewritten software, will probably cause computers to be used exclusively for the prediction of non-linear system response.

APPENDIX

APPENDIX I

Numerical Integration

Program THESIS reads in physical parameters including inlet conditions. It then calls routine CINT.

Routine CINT searches large ranges of temperature for the heat balance equation to change sign. When a sign change is found it lists the root of the equation under steady state points. The heat balance equation and the steady state concentrations are evaluated in routine FCT.

Program THESIS then reads the initial temperature and concentrations. In a section called subroutine RKGS, the initial conditions are listed, the derivatives evaluated and the equations integrated using a fourth order Runge-Kutta method. In a section called FCT, the derivatives are calculated. A section called OUTP is used to output results.

```
OGRAM    THESIS   FORTRAN EXTENDED VERSION 2.0          05/07/71

      PROGRAM THESIS(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      DIMENSION Y(2),DERY(3),AUX(3,4),A(4),B(4),C(4),PRMT(5)
      COMMON VR,DELH,CP,U,AR,RHO,DELE,TC,G,CAI,CRI,TI,K
C
C     MAIN PROGRAM
C
      REAL K
      LI=5
      LO=6
      K=1,
C
C     READ PARAMETERS
C
      READ(LI,102)VR,DELH,CP,U,AR,RHO,DELE,TC
  995 READ(LI,102)G,CAI,CRI,TI,K
  102 FORMAT(8F10.7)
      DO 99 JJ=1,100
      WRITE(LO,93)
   93 FORMAT(1HJ)
      DELH=-ABS(DELH)
      K=1,2556+12
      RT=12,
C
C     SET INITIAL CONDITIONS
C
      READ(LI,92)Y,G
   92 FORMAT(*E10.4)
      CALL CIRT(Y)
C
C     SUBROUTINE RKGS
C
      PRMT(1)=0,
      PRMT(2)=RT
      PRMT(3)=.2
      PRMT(4)=1.E+10
      DERY(1)=1./2001,
      DERY(2)=3000./2001,
      DERY(3)=1000./2001,
      NO1M=3
      DO 1 I=1,NO1M
    1 AUX(3,I)=.0E0000007*DERY(I)
      X=PRMT(1)
      XEND=PRMT(2)
      H=PRMT(3)
      PRMT(5)=0,
C     CALL FCT(X,Y,DERY)
  999 NCAL=2
      GO TO 200
  201 CONTINUE
C
C     ERROR TEST
C
      IF(4*(XEND-X))33,37,2
```

```
ROGRAM     THESIS   FORTRAN EXTENDED VERSION 2.0          05/07/71
C
C     PREPARATIONS FOR RUNGE-KUTTA METHOD
C
      2 A(1)=.5
        A(2)=.29289322
        A(3)=1.7071067
        A(4)=.16666667
        B(1)=2.
        B(2)=1.
        B(3)=1.
        B(4)=2.
        C(1)=.5
        C(2)=.29289322
        C(3)=1.7071067
        C(4)=.5
C
C     PREPARATIONS OF FIRST RUNGE-KUTTA STEP
C
        DO 3 I=1,NDIM
        AUX(1,I)=Y(I)
        AUX(2,I)=DERY(I)
        AUX(3,I)=0.
      3 AUX(4,I)=0.
        IREC=0
        H=H+H
        IHALF=-1
        ISTEP=0
        IEND=0
C
C     START OF A RUNGE-KUTTA STEP
C
      4 IF((X+H-XEND)*H)7,6,5
      5 H=XEND-X
      6 IEND=1
C
C     RECORDING OF INITIAL VALUES OF THIS STEP
C
C     7 CALL OUTP(X,Y,DERY,IREC,NDIM,PRMT)
      7   LOCAL=1
          GO TO 301
    301   CONTINUE
      8 ITEST=0
      9 ISTEP=ISTEP+1
C
C     START OF INNERMOST RUNGE-KUTTA LOOP
C
        J=1
     10 AJ=A(J)
        BJ=B(J)
        CJ=C(J)
        DO 11 I=1,NDIM
        R1=H*DERY(I)
        R2=AJ*(R1-BJ*AUX(3,I))
```

```
PROGRAM    THESIS   FORTRAN EXTENDED VERSION 4.0          05/07/71
                    Y(I)=Y(I)+KP
                    KP=KP+KP+KP
                 11 AUX(6,I)=AUX(6,I)+KP+CJ*K1
                    IF(J-4)12,15,15
                 12 J=J+1
                    IF(J-3)13,14,13
                 13 X=X+.5*H
              C  14 CALL FCT(X,Y,DERY)
                    NCAL=3
                    GO TO 200
                 203 CONTINUE
                    GOTO 10
              C
              C     END OF INNERMOST RUNGE-KUTTA LOOP
              C
              C     TEST OF ACCURACY
                 15 IF(ITEST)16,16,30
              C
              C     IN CASE ITEST=0 THERE IS NO POSSIBILITY FOR TESTING OF ACCURACY
              C
                 16 DO 17 I=1,NDIM
                 17 AUX(4,I)=Y(I)
                    ITEST=1
                    ISTEP=ISTEP+ISTEP=2
                 18 IHLF=IHLF+1
                    X=X-H
                    H=.5*H
                    DO 19 I=1,NDIM
                    Y(I)=AUX(1,I)
                    DERY(I)=AUX(2,I)
                 19 AUX(6,I)=AUX(3,I)
                    GOTO 9
              C
              C     IN CASE ITEST=1 TESTING OF ACCURACY IS POSSIBLE
              C
                 20 IMOD=ISTEP/2
                    IF(ISTEP-INCU-IMOD)21,23,21
              C  21 CALL FCT(X,Y,DERY)
                 21    NCAL=3
                    GO TO 200
                 203 CONTINUE
                    DO 22 I=1,NDIM
                    AUX(5,I)=Y(I)
                 22 AUX(7,I)=DERY(I)
                    GOTO 9
              C
              C     COMPUTATION OF TEST VALUE DELT
              C
                 23 DELT=0.
                    DO 24 I=1,NDIM
                 24 DELT=DELT+AUX(8,I)*ABS(AUX(4,I)-Y(I))
                    IF(DELT-PRMT(4))28,28,25
              C
```

```
C       ERROR IS TOO GREAT
C
   25 IF(IHLF-10)26,36,36
   26 DO 27 I=1,NDIM
   27 AUX(7,I)=AUX(5,I)
      ISTEP=ISTEP+ISTEP
      X=X-H
      IEND=0
      GOTO 12
C
C       RESULT VALUES ARE GOOD
C
C  28 CALL FCT(X,Y,DERY)
   28 NCAL=4
      GO TO 200
  204 CONTINUE
      DO 29 I=1,NDIM
      AUX(1,I)=Y(I)
      AUX(2,I)=DERY(I)
      AUX(3,I)=AUX(5,I)
      Y(I)=AUX(5,I)
   29 DERY(I)=AUX(7,I)
C       CALL OUTP(X-H,Y,DERY,IHLF,NDIM,PRMT)
      LCAL=2
      X=X-H
      GO TO 300
  302 CONTINUE
      X=X+H
   30 DO 31 I=1,NDIM
      Y(I)=AUX(1,I)
   31 DERY(I)=AUX(2,I)
      IREC=IHLF
      IF(IEND)32,32,40
C
C       INCREMENT GETS DOUBLED
C
   32 IHLF=IHLF-1
      ISTEP=ISTEP/2
      H=H+H
      IF(IHLF)4,33,33
   33 IMOD=ISTEP/2
      IF(ISTEP-IMOD-IMOD)34,34,4
   34 IF(DELT-.02*PRMT(4))35,35,4
   35 IHLF=IHLF-1
      ISTEP=ISTEP/2
      H=H+H
      GOTO 4
C
C       RETURNS TO CALLING PROGRAM
C
   36 IHLF=11
C       CALL FCT(X,Y,DERY)
      WRITE(LO,1131)X
```

```
PROGRAM   THESIS   FORTRAN EXTENDED VERSION 2.0          05/07/71
     1A3A  FORMAT(1HC,5EX,26HINTEGRATION FAILED ,5X,8HAT TIME=,F10.4)
           LCAL=1
           GO TO 400
      345  CONTINUE
           GOTO 39
        37 IHLF=12
           GOTO 39
        38 IHLF=13
C       39 CALL OUTP(X,Y,DERY,IHLF,NDIM,PRMT)
        39 LCAL=3
           GO TO 370
C
C          SUBROUTINE FCT(X,Y,DERY)
C          ------------------------------------------------------------
      200  CONTINUE
C
C          CHECK FOR UNREALISTIC CONDITIONS
C
           IF(Y(1).GE.1.E+50 )GO TO 1121
           IF(Y(1).LE.10.)Y(1)=10.
C
C          CALCULATE DERIVATIVES
C
           DERY(1)=(-DELH*VR*K*Y(2)*Y(3)*EXP(-DELE/R/Y(1))-RHO*Q*CP*(Y(1)-TI
          1        -U*AR*(Y(1)-TC))/(RHO*VR*CP)
           DERY(2)=-K*Y(2)*Y(3)*EXP(-DELE/R/Y(1))-Q/VR*(Y(2)-CAI)
           DERY(3)=K*Y(2)*Y(3)*EXP(-DELE/R/Y(1))-Q/VR*(Y(3)-CRI)
           GO TO(201,202,203,204,205),NCAL
     1121  WRITE(LO,1122)
     1122  FORMAT(1HO,50X,16HREACTOR EXPLODED //)
           LCAL=3
           GO TO 400
C
C          SUBROUTINE OUTP
C          ------------------------------------------------------------
      300  CONTINUE
           XOP=X
      400  WRITE(LO,878)X,Y(1),Y(2),Y(3),IHLF
      878  FORMAT(1HO,8HAT TIME=,F12.2,5X,5HTEMP=,E15.6,5X,7HCONC.A=,E15.6,
          1   5X,7HCONC.B=,E15.6,5X,I5)
           AAA=K*Y(2)*Y(3)*EXP(-DELE/R/Y(1))
           BBB=Q/VR*(Y(2)-CAI)
           WRITE(LO,987)DERY,AAA,BBB
      987  FORMAT(1HO,11HD(TEMP)/DT=,E11.4,5X,7HDCA/DT=,E11.4,5X,7HDCB/DT=,
          1 E11.4,5X,7HA-PROD=,E11.4,5X,7HA-LOST=,E11.4)
           YOLD=Y(1)
      340  GO TO (301,302,59),LCAL
C
C          TERMINATING ROUTINES
C          ------------------------------------------------------------
       59  CONTINUE
       58  CALL EXIT
           END
```

```
SROUTINE  CINT     FORTRAN EXTENDED VERSION 2.0                  05/07/71
                   SUBROUTINE CINT(Y)
                   DIMENSION Y(3)
                   COMMON VR,DELH,CP,U,AR,RHO,DELE,TC,G,CAT,CRI,TI,K
                   CRSS=1.
                   WRITE(6,25)
             25    FORMAT(1H ,20X,29HNEGATEAUV STATE POINTS ARE= )
                   TLS=Y,
                   TRS=0.
                   DO 3 J=1,500
                   XLS=TLS
                   XRS=TRS
                   SL=FCT(TLS,CRSS)
                   SR=FCT(TRS,CRSS)
                   IF(SIGN(1.,SL).EQ.SIGN(1.,SR))GO TO 55
             3     DO 10 I=1,50
                   IF(XRS-XLS.LT..0001)GO TO 15
                   XM=(XLS+XRS)/2.
                   SL=FCT(XLS,CRSS)
                   SR=FCT(XRS,CRSS)
                   SM=FCT(XM,CRSS)
                   IF(SIGN(1.,SL).EQ.SIGN(1.,SM))XLS=XM
                   IF(SIGN(1.,SR).EQ.SIGN(1.,SM))XRS=XM
                   IF(SIGN(1.,SL).EQ.SIGN(1.,SR))GO TO 66
            10     CONTINUE
                   GO TO 67
            15     AA=CAI+CAT-CRSS
                   WRITE(6,165) XM,AA,CRSS
           165     FORMAT(1H ,20X,7HMTSS=,E15.6,10X,5HCASS=,E15.6,10X,5HCRSS=,E15.6
                   GO TO 60
            66     WRITE(6,166)
           166     FORMAT(13H TWO ROOTS)
                   XRS=XM
                   GO TO 3
            67     WRITE(6,167)
           167     FORMAT(8H NO ROOT)
            60     TLS=TLS++.
           200     TRS=TRS++.
                   RETURN
                   END
```

```
UNCTION    FCT      FORTRAN EXTENDED VERSION 2.0                    05/07/71

           FUNCTION FCT(TSS,CRSS)
           REAL K
           COMMON VR,DELH,CP,U,AR,RHO,BELE,TC,Q,CAI,CRI,TI,K
           K=4.
           AA=      EXP(-BELE/R/TSS)
           A=(2*K*Q*AA
           IF(A.LE.0.)A=1.E-100
           B=N*R-CAI*A-CRI*A
           C=-K*Q*CRI
           CRSS=0.
           IF(B*B-4.*A*C)10,20,30
   10      WRITE(6,15)A,B,C
   15      FORMAT(1H ,10HIMAG, ROOT,3E15.6)
           GO TO 25
   20      CRSS=-B/(A+A)
           GO TO 35
   30      CRSS=(-B+SQRT(B*B-4.*A*C))/(A+A)
   35      FCT=-DELH*(Q*CRSS-Q*CRI)-RHO*Q*CP*(TSS-TI)-U*AR*(TSS-TC)
   55      RETURN
           END
```

START OF NEW CALCULATION

TSTAR= 3.0000E+02 ALPHA= 1.5947E+08 BETA= 1.6566E+00 GAMMA= 1.0000E+00 DELTA= 2.813

STEADY STATE POINTS ARE-

TSS=	3.000008E+02	CASS=	1.000000E-02	CRSS=	1.000001E-04
TSS=	6.430840E+02	CASS=	3.096494E-03	CRSS=	7.003506E-03
TSS=	7.819450E+02	CASS=	3.023204E-04	CRSS=	9.797680E-03

AT TIME= 0.00 TEMP= 8.400000E+02 CONC.A= 1.000000E-03 CONC.R= -0.

D(TEMP)/DT=-4.2497E+06 DCA/DT= 7.0829E+01 DCR/DT= 7.8699E-01 A-PROD= 0. A-LOST=-7

TBAR= 2.800000E+00 CABAR= 1.000000E-01 CRBAR= 0.

AT TIME= .00 TEMP= 5.485041E+02 CONC.A= 5.853118E-03 CONC.R= 8.422901E-05

D(TEMP)/DT=-1.9493E+06 DCA/DT= 3.2507E+01 DCR/DT= 2.5261E-01 A-PROD= 1.2849E-01 A-LOST=-3.

TBAR= 1.828347E+00 CABAR= 5.853118E-01 CRBAR= 8.422901E-03

AT TIME= .00 TEMP= 4.137462E+02 CONC.A= 8.101627E-03 CONC.R= 9.423267E-05

D(TEMP)/DT=-8.9510E+05 DCA/DT= 1.4939E+01 DCR/DT= 4.6713E-02 A-PROD= 1.3251E-03 A-LOST=-1

TBAR= 1.379154E+00 CABAR= 8.101627E-01 CRBAR= 9.423267E-03

AT TIME= .00 TEMP= 3.520324E+02 CONC.A= 9.131600E-03 CONC.R= 9.738036E-05

D(TEMP)/DT=-4.0948E+05 DCA/DT= 6.8341E+00 DCR/DT= 2.0659E-02 A-PROD= 4.3194E-05 A-LOST=-6.

TBAR= 1.173441E+00 CABAR= 9.131600E-01 CRBAR= 9.738036E-03

AT TIME= .00 TEMP= 3.238014E+02 CONC.A= 9.602763E-03 CONC.R= 9.880267E-05

AT TIME= .00 TEMP= 3.108876E+02 CONC.A= 9.818290E-03 CONC.R= 9.945251E-05

D(TEMP)/DT=-8.5684E+04 DCA/DT= 1.4300E+00 DCR/DT= 4.3107E-03 A-PROD= 1.9863E-06 A-LOST=-1

TBAR= 1.036292E+00 CABAR= 9.818290E-01 CRBAR= 9.945251E-03

AT TIME= .00 TEMP= 3.049804E+02 CONC.A= 9.916879E-03 CONC.R= 9.974966E-05

D(TEMP)/DT=-3.9195E+04 DCA/DT= 6.5415E-01 DCR/DT= 1.9714E-03 A-PROD= 1.1893E-06 A-LOST=-6

TBAR= 1.016601E+00 CABAR= 9.916879E-01 CRBAR= 9.974966E-03

AT TIME= .00 TEMP= 3.022782E+02 CONC.A= 9.961978E-03 CONC.R= 9.988555E-05

D(TEMP)/DT=-1.7929E+04 DCA/DT= 2.9923E-01 DCR/DT= 9.0161E-04 A-PROD= 9.3417E-07 A-LOST=-2

TBAR= 1.007594E+00 CABAR= 9.961978E-01 CRBAR= 9.988555E-03

AT TIME= .00 TEMP= 3.010421E+02 CONC.A= 9.982607E-03 CONC.R= 9.994771E-05

D(TEMP)/DT=-8.2014E+03 DCA/DT= 1.3688E-01 DCR/DT= 4.1236E-04 A-PROD= 8.3523E-07 A-LOST=-1

TBAR= 1.003474E+00 CABAR= 9.982607E-01 CRBAR= 9.994771E-03

AT TIME= .00 TEMP= 3.004767E+02 CONC.A= 9.992044E-03 CONC.R= 9.997614E-05

D(TEMP)/DT=-3.7516E+03 DCA/DT= 6.2613E-02 DCR/DT= 1.8860E-04 A-PROD= 7.9328E-07 A-LOST=-6

TBAR= 1.001589E+00 CABAR= 9.992044E-01 CRBAR= 9.997614E-03

AT TIME= .00 TEMP= 3.002181E+02 CONC.A= 9.996361E-03 CONC.R= 9.998914E-05

D(TEMP)/DT=-1.7161E+03 DCA/DT= 2.8641E-02 DCR/DT= 8.6261E-05 A-PROD= 7.7475E-07 A-LOST=-2

APPENDIX II

Linearization

Program LONA reads in the steady state temperature and concentrations and the flow rate at which they were obtained. It calculates the partial derivatives of the rate expression "G" with respect to the three state variables. It then evaluates the A matrix and calls a subroutine TRANS.

TRANS calculates the state transition matrix $\Phi(+)$ using the relation

$$\Phi(t) = I + At + \frac{A^2 t^2}{2!} + \ldots\ldots$$

For initial conditions, within five decimal places of steady state, TRANS outputs the unforced response. If it dies out, the steady state point is assummed stable.

```
PROGRAM  LONG        FORTRAN EXTENDED VERSION 2.0          05/07/71
      PROGRAM LONG(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      DIMENSION A1(3,3),A2(3,3),A3(3,3)
      WRITE(6,5)
    5 FORMAT(1H1)
    4 READ(5,1)TSS,CABSS,CRBSS,E
    1 FORMAT(7E11.3)
      A =,22D*E,
      CABSS=CABSS*1.E-6,
      CRBSS=CRBSS*1.E-6,
      B=2.,
      D=1.E-6,
      F=.7D,
      XP=EXP(-D*TSS/TSS)
      G1=1.,0E-2*L+12.*CABSS*CRBSS*XP*300./(TSS*TSS)
      G2=1.,85E-2+D*CRBSS*XP
      G3=1.,85E-2+D*CABSS*XP
      A11=-B+A*G1
      A21=-D*C1
      A31=F*G1
      A12=A*G2
      A22=E-D*G2
      A32=F*G2
      A13=A*G3
      A23=E+F*G3
      A33=D*G3
      A1(1,1)=A11
      A1(1,2)=A12
      A1(1,3)=A13
      A1(2,1)=A21
      A1(2,2)=A22
      A1(2,3)=A23
      A1(3,1)=A31
      A1(3,2)=A32
      A1(3,3)=A33
      WRITE(6,2)TSS,CABSS,CRBSS,A
    2 FORMAT(//5X,7E11.3)
      CALL TRANS(A1)
      GO TO 4
    6 CALL EXIT
      END
```

```
SUBROUTINE TRANS    FORTRAN EXTENDED VERSION 2.0                08/07/71
                    SUBROUTINE TRANS(A)
                    DIMENSION A(3,3),B(3,3),C(3,3),D(3,3),X(3),Y(3)
                    T=1.E-05
                    DO 1 I=1,3
                    DO 1 J=1,3
                    A(I,J)=T*A(I,J)
                    C(I,J)=0.
                    D(I,J)=A(I,J)
                  1 B(I,J)=A(I,J)
                    DO 5 IK=2,50
                    DO 4 I=1,3
                    DO 4 J=1,3
                    DO 4 K=1,3
                  4 C(I,J)=C(I,J)+A(I,K)*B(K,J)/IK
                    DO 5 I=1,3
                    DO 5 J=1,3
                    B(I,J)=C(I,J)
                    D(I,J)=D(I,J)+C(I,J)
                  5 C(I,J)=0.
                  6 CONTINUE
                    DO 10 I=1,3
                 10 C(I,I)=1.
                    DO 20 I=1,3
                    DO 20 J=1,3
                 20 D(I,J)=D(I,J)+C(I,J)
                    Y(1)=.001
                    Y(2)=.001
                    Y(3)=.002
                    DO 400 L=1,10
                    DO 101 I=1,3
                    X(I)=0.
                    DO 101 J=1,3
                101 X(I)=X(I)+D(I,J)*Y(J)
                    DO 200 K=1,3
                200 Y(K)=X(K)
                    WRITE(6,66)Y
                 66 FORMAT(1X,3E10.5)
                400 CONTINUE
                    RETURN
                    END
```

T_{ss}	$\bar{C}_{Ass}$	$\bar{C}_{Rss}$	Q
3,0000E+02	1,0000E+00	1,1172E-02	1,0000E+01
	9,9705E-01	9,9941E-01	9,9911E-01
	9,9525E-01	9,9720E-01	9,9801E-01
X(+)	9,9331E-01	9,9507E-01	9,9701E-01
	9,9150E-01	9,9296E-01	9,9601E-01
	9,8950E-01	9,9086E-01	9,9501E-01
	9,8750E-01	9,8876E-01	9,9401E-01
	9,8550E-01	9,8666E-01	9,9301E-01
	9,8350E-01	9,8456E-01	9,9201E-01
	9,8150E-01	9,8246E-01	9,9101E-01

7,9647E+02	3,5234E-10	1,1013E+00	1,0000E+06
	-2,1324E+52	4,3699E+37	-4,3699E+57
	-3,3519E+11	1,9626E+11	-1,9096E+11
	-1,3561E+10	2,3477E+17	-2,3477E+17
	-6,7965E+01	3,6455E+09	-3,6456E+09
	-2,3529E+01	1,5938E+00	-1,5935E+00

APPENDIX III

Lyapunov Functions

Program LYAP outputs the reference temperature used and then calculates the corresponding state variable X_1. For an initial value of K, it calculates a Lyapunov Function. It searches for the crossing the axis by the function and divides each quadrant in five sections, each equally spaced apart. Points on the Lyapunov function are calculated in each section. On points corresponding to positive concentration, the program tests the matrix

$$\dot{F} = \left(\frac{\partial f}{\partial x}\right)^T P + P\frac{\partial f}{\partial x} + Q$$

for being negative definite. If it is, K is incremented, another Lyapunov Function is calculated, and the process is repeated. Once the matrix $\dot{F}$ is no longer negative definite, the program points out the Lyapunov Function which caused this to happen and prints a message that the reactor exploded.

```
PROGRAM    LYAP     FORTRAN EXTENDED VERSION 2.0          05/07/71
      PROGRAM LYAP(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      REAL L
      DIMENSION CAB(20),CAB(20)
      DIMENSION X3U(2),AX2(20),AX3(20)
      DIMENSION TREF(5)
      DATA TREF/.005,.0H0,.720,.9U0,.9H0,/
      GLF(X1,X2,X3)=(X1+,H30+)*(X3+1,3594)/((X1+,0+19)*(X1+,0+19))
     1  *,7L5+E+00*EXP(-1+,867/(X1+,0+19))
      GEF(X1,X2,X3)=1,000E+06 *(X3+1,3594)*EXP(-1+,867/(X1+,0+19))
      GBF(X1,X2,X3)=0U2*(X3+,630+)/(X3+1,3594)
      GF(X1,X2,X3)=(X3+1,3594)*(X2+,630+)*1,E0+6  *EXP(-1+,867/(X1+,0+1
     1   ))-,72+
      VF(X1,X2,X3)=1,79*(A*X1-A*G)**2+4,73*(X2+0*G)**2+(X3-0*G)**2
      A=,139
      G=1,0
      D=,5
      L=1,
      F=0
      JL=2
      WRITE(6,790)TREF(JL)
  790 FORMAT(1H1//4HX,5HTREF=,F10,0)
      X1=TREF(JL)/710,-,0+19
      K=1,
    3 XRS3=1000,
      DO 5 L=1,2
      X2=0,
      XLS3=0,
      DO 5 I=1,20
      XM=(XLS3+XRS3)/2,
      G  =GF(X1,X2,XLS3)
      GOPT=G
      VL=VF(X1,X2,XLS3)-K
      G  =GF(X1,X2,XRS3)
      VR=VF(X1,X2,XRS3)-K
      G  =GF(X1,X2,XM)
      VM=VF(X1,X2,XM)-K
      IF(SIGN(1.,VL).NE.SIGN(1.,VM))XRS3=XM
      IF(SIGN(1.,VR).NE.SIGN(1.,VM))XLS3=XM
      IF(SIGN(1.,VR).EQ.SIGN(1.,VL))XRS3=0.
    5 CONTINUE
      X3U(L)=XM
    6 XRS3=-1000.
      DO 8 I=1,5
      AX3(I)=X30(1)*I/5
      AX3(I+10)=AX3(I)
      AX3(I+5 )=X30(2)*I/5
    8 AX3(I+15)=AX3(I+5 )
      DO 10 L=1,20
      SG=1.
      IF(L.GT.10)SG=-1.
      XLS2=0.
      XRS2=1000.*SG
      X3=AX3(L)
```

```
PROGRAM  LYAP   FORTRAN EXTENDED VERSION 2.2                    05/07/71
      DO 12 I=1,20
      XM=(XLSM+XLSE)/2.
      V=VF(X1,XLSE,X3)
      VL=VF(X1,XLSE,X3)-K
      G=GF(X1,XRSP,X3)
      VR=VF(X1,XRSP,X3)-K
      G=GF(X1,XM,X3)
      VM=VF(X1,XM,X3)-K
      IF(SIGN(1.,VL).NE.SIGN(1.,VM))XRSP=XM
      IF(SIGN(1.,VR).NE.SIGN(1.,VM))XLSE=XM
      IF(SIGN(1.,VR).EQ.SIGN(1.,VL))XRSP=0.
   12 CONTINUE
   13 AX1(L)=XM
      DO 14 I=1,20
      X2=AX2(I)
      X3=AX3(I)
      IF(X2.LE.0..OR.X3.LE.0.)GO TO 15
      G1=G1F(X1,X2,X3)
      G2=G2F(X1,X2,X3)
      G3=G3F(X1,X2,X3)
      G=GF(X1,X2,X3)
      A11=3.59*(A*G1-R)
      A22=9.4*(-E-D*G2)
      A33=2.*(-E-F*G3)
      C1=A11
      C2=A11*A22
      C3=A11*A22*A33
      IF(C1.GE.0.)GO TO 20
   15 CONTINUE
      DO 479 IH=1,20
      CAB(IH)=AX2(IH)+.630+
      CRB(IH)=AX3(IH)+1.359+
  479 CONTINUE
      WRITE(6,25)CAB,CRB,K,C1,C2,C3,G,G1,G2,G3
      K=K+3000.
      IF(K.GT.25000.)GO TO 26
      GO TO 2
   20 DO 478 IH=1,20
      CAB(IH)=AX2(IH)+.630+
      CRB(IH)=AX3(IH)+1.359+
  478 CONTINUE
      WRITE(6,25)CAB,CRB,K,C1,C2,C3,G,G1,G2,G3
   25 FORMAT(
     1      //5X,14HCA-POINTS ARE=,10F 8.3/19X,10F 8.3/
     1   5X,14HCR POINTS ARE=,10F 8.3/19X,10F 8.3/5X,2HK=,F9.1,5X,3HC1=,
     A F10.2,5X,3HC2=,F10.2,5X,3HC3=,
     BF10.2/5X,2HG=,F10.5,5X,3HG1=,F10.5,5X,3HG2=,F10.5,5X,3HG3=,F10.5)
   26 WRITE(6,37)
   37 FORMAT(//15X,24H*** REACTOR EXPLODED *** )
   38 CALL EXIT
      END
```

TREF= 630

CA-POINTS ARE=	.63040	.63040	.63040	.63040	.63040	.63040	.63040	.63040	.63040
	.63040	.63040	.63040	.63040	.63040	.63040	.63040	.63040	.63040
CR POINTS ARE=	1.36940	1.36940	1.36940	1.36940	1.36940	1.36940	1.36940	1.36940	1.36940
	1.36940	1.36940	1.36940	1.36940	1.36940	1.36940	1.36940	1.36940	1.36940

K= 1.0 C1= -3.82 C2= 36.68 C3= -73.62
G= 3.37908 G1= .95525 G2= .04243 G3= .00728

CA-POINTS ARE=	.63040	.63040	.63040	.63040	.63040	.63040	.63040	.63040	.63040
	.63040	.63040	.63040	.63040	.63040	.63040	.63040	.63040	.63040
CR POINTS ARE=	1.36940	1.36940	1.36940	1.36940	1.36940	1.36940	1.36940	1.36940	1.36940
	1.36940	1.36940	1.36940	1.36940	1.36940	1.36940	1.36940	1.36940	1.36940

K= 11.0 C1= -3.82 C2= 36.68 C3= -73.62
G= 3.37908 G1= .95525 G2= .04243 G3= .00728

CA-POINTS ARE=	.67522	.66378	.65233	.64089	.63040	.98803	1.87876	6.87029	1.39429
	-.35856	-.35093	-.34330	-.33567	.63040	-.55692	-1.02232	-2.51959	-1.07191
CR POINTS ARE=	1.40697	1.44455	1.48212	1.51970	1.55727	.77946	.18951	-.40043	-.99037
	1.40697	1.44455	1.48212	1.51970	1.55727	.77946	.18951	-.40043	-.99037

K= 21.0 C1= -2.39 C2= 25.37 C3= -53.52
G= 3.82184 G1= 3.83338 G2= .26003 G3= .10966

CA-POINTS ARE=	.76105	.72291	.68857	.65806	.63135	1.23026	2.88012	4.41744	1.16732
	-.45202	-.42341	-.39861	-.37573	-.35475	-.77627	-1.69180	-2.80569	-.98799
CR POINTS ARE=	1.47984	1.59027	1.70071	1.81114	1.92158	.70621	.04303	-.62016	-1.28334
	1.47984	1.59027	1.70071	1.81114	1.92158	.70621	.04303	-.62016	-1.28334

CA-POINTS ARE=	.93081	.82972	.74961	.68476	.63135	1.91500	8.78718	2.16105	.98994
	-.63703	-.55311	-.48826	-.43295	-.38717	-1.39044	-5.14601	-1.92259	-.86401
CR POINTS ARE=	1.64387	1.91833	2.19280	2.46727	2.74174	.54218	-.28503	-1.11225	-1.93947
	1.64387	1.91833	2.19280	2.46727	2.74174	.54218	-.28503	-1.11225	-1.93947
K= 61.0	C1= -.91	C2= 10.51	C3= -22.16						
G= 6.85002	G1= 6.81301	G2= .46914	G3= .10803						

CA-POINTS ARE=	.97277	.85451	.76296	.69048	.63135	2.14388	10.86237	1.97603	.96514
	-.68090	-.58363	-.50543	-.44439	-.39289	-1.59452	-6.48306	-1.78907	-.84303
CR POINTS ARE=	1.68850	2.00760	2.32670	2.64580	2.96490	.49755	-.37430	-1.24615	-2.11800
	1.68850	2.00760	2.32670	2.64580	2.96490	.49755	-.37430	-1.24615	-2.11800
K= 71.0	C1= -.63	C2= 7.42	C3= -15.64						
G= 7.41360	G1= 7.36755	G2= .50732	G3= .10803						

CA-POINTS ARE=	1.01092	.87549	.77440	.69430	.63135	2.37849	10.86809	1.85015	.94797
	-.72286	-.60842	-.52259	-.45393	-.39861	-1.80052	-7.05526	-1.68989	-.82586
CR POINTS ARE=	1.73008	2.09076	2.45144	2.81212	3.17280	.45597	-.45746	-1.37089	-2.28432
	1.73008	2.09076	2.45144	2.81212	3.17280	.45597	-.45746	-1.37089	-2.28432
K= 81.0	C1= -.37	C2= 4.45	C3= -9.39						
G= 7.93863	G1= 7.88416	G2= .54289	G3= .10803						

CA-POINTS ARE=	1.04525	.89457	.78394	.69811	.63040	2.61881	9.44330	1.75860	.93462
	-.75910	-.63131	-.53594	-.46156	.63040	-2.01414	-6.80921	-1.61360	-.81251
CR POINTS ARE=	1.76937	2.16934	2.56931	2.96928	3.36926	.41706	-.53528	-1.48762	-2.43996
	1.76937	2.16934	2.56931	2.96928	3.36926	.41706	-.53528	-1.48762	-2.43996
K= 91.0	C1= -.24	C2= 2.78	C3= -5.90						
G= 8.21756	G1= 8.15862	G2= .50807	G3= .11945						

CA-POINTS ARE=	1.07767	.91173	.79157	.70193	.63135	2.86677	7.95557	1.68802	.92318
	-.79344	-.65038	-.54739	-.46728	-.40434	-2.23348	-6.23892	-1.55256	-.80107
CR POINTS ARE=	1.80599	2.24258	2.67918	3.11577	3.55236	.38006	-.60928	-1.59863	-2.58797
	1.80599	2.24258	2.67918	3.11577	3.55236	.38006	-.60928	-1.59863	-2.58797
K= 101.0	C1= .10	C2= -1.18	C3= 2.50						
G= 8.89718	G1= 8.82735	G2= .60784	G3= .10803						

*** REACTOR EXPLODED ***

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